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SO2 Oxidation in Plumes: A Review and Assessment of Relevant Mechanistic and Rate Studies

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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SO_2 OXIDATION IN PLUMES: A REVIEW AND ASSESSMENT OF RELEVANT MECHANISTIC AND RATE STUDIES

by

A. Levy, D.R. Drewes, and J.M. Hales

Battelle Pacific Northwest Laboratories
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Richland, Washington 99352

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16. ABSTRACT

The scientific literature pertaining to the oxidation of SO_2 in power plant plumes is reviewed. Aqueous phase, homogeneous gas phase, and heterogeneous gas phase mechanisms are considered, as are actual plume studies. The reported rates vary over a wide range, which is not totally unexpected due to the highly complex nature of the oxidation process, and some general conclusions can be drawn:

1) Recent plume studies, in general, indicate lower rates than earlier ones, and also suggest a coincidence between the reappearance of ozone in the plume and oxidation of SO_2.

2) Gas phase studies indicate homogeneous reaction of SO_2 with OH radicals and heterogeneous reactions catalyzed by lead and iron to be perhaps the most significant processes.

3) In the aqueous phase, the reaction is most effectively catalyzed by iron and manganese, and ammonia plays an important role in promoting the oxidation by maintaining a high pH.

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SECTION I

CONCLUSIONS

The available literature concerning the oxidation of SO_2 in plumes does not allow firm quantitative conclusions to be drawn concerning absolute rates or mechanisms. Reported rates cover a wide range, and few details of the relevant mechanisms are well established. Despite these uncertainties, however, one can state with some confidence several characteristics of in-plume SO_2 conversion processes. It is known, for example, that many factors strongly influence the rate of oxidation of SO_2. The evidence collected thus far indicates that the gas phase oxidation rate increases with increasing relative humidity. The concentrations of catalysts (in the case of heterogeneous oxidation) and reactive species (for homogeneous oxidation) also exert a profound influence on the rate. In aqueous systems, pH, temperature, and catalyst concentration are perhaps the most significant factors in determining the oxidation rate. Furthermore, several complex mechanisms may be involved in the oxidation under various conditions. Indeed, considering the magnitude of the problem, it would be extremely fortuitous if a single rate expression could be applied under all meteorological conditions and all ambient atmospheres for all plumes generated by all types and grades of fossil fuels. This, however, is little comfort to the modeller, whose job it is to reduce the complex system to a managable number of variables, relate these variables with a sound mathematical formalism and perform calculations to yield results which conform qualitatively and (hopefully) quantitatively to the actual situation existing in the atmosphere.

Unfortunately, the development of an entirely general model is highly impractical. It may, however, be possible to model various specific situations with a degree of success by using available data with appropriate parameterizations, the nature of which will depend upon the exact requirements of the model.

The oxidation of SO_2 has been studied both in the laboratory and in the field. The results of those studies are divided into four broad classifications and summarized below.

Plume Studies

1) Measured SO_2 oxidation rates range from 0 to 55%/hr. The dependence of the rate on meteorological variables, especially relative humidity, is recognized, but there is no way to control these variables in field experiments.
2) Recent studies indicate lower rates than previously reported, but as yet only one study has measured sulfate formation directly.
3) It is recognized that the rate of oxidation varies spacially in the plume; the results of one study, however, indicate a high rate near the stack and a lower rate downwind, while another suggests the opposite situation.
4) Two recent studies indicate a correlation between ozone in the plume and the oxidation of SO_2, with the oxida-

tion rate increasing downwind as ozone returns to ambient levels after having been depleted by reaction with NO in the early plume.

5) Hydrocarbons may promote SO_2 oxidation *via* photochemical smog processes.

Homogeneous Gas Phase Studies

1) Rates are expected to be from 1.6 to 13.3%/hr.
2) Evidence indicates that the reaction of SO_2 with OH may be the most significant process in the atmosphere, but OH levels in plumes are not known precisely.

Aqueous Phase Studies

1) Reported rates range from 0 to 20%/hr.
2) Dissolved manganese and iron are the most efficient catalysts, and both species are expected to be present in plumes.
3) Hydration of aerosols, particularly manganese sulfate, can form an aqueous phase capable of oxidizing SO_2 at an appreciable rate.

Heterogeneous Studies

1) Oxidation rates range from 0 to 6%/hr.
2) Lead and iron are efficient catalysts promoting high reaction rates; vanadium, surprisingly, appears to be an inefficient catalyst in plumes.

It cannot be overemphasized that the oxidation of SO_2 in the atmosphere is a highly complex process, and that the rate is and should be highly dependent on the nature of the plume and the existing meteorological conditions. Because of the extreme variability of data pertaining to atmospheric SO_2 oxidation processes, it is difficult to provide any meaningful recommendation on rate expressions to be used for practical modeling purposes. It can be stated with some certainty, however, <u>that insofar as modeling for scoping purposes is concerned</u>, the results available thus far do not justify the application of rate expressions any more elaborate than the psuedo-first order form $\frac{d(SO_2)}{dt} = - k\ (SO_2)$.

Since SO_2 oxidation processes are typically highly complex, they will not be expected to adhere to the above linearized expression accurately over extensive ranges of conditions. The basically unsatisfactory state of this field, however, leaves us with little reasonable choice but to proceed with this approach. Recognizing these factors, and with a warning against indiscriminate use, it is suggested that, for general purposes of model calculations, first order SO_2 oxidation rates in the range 0.5 to 10%/hr are consistent with the bulk of the literature, and a reasonable value for many situations is 2%/hr. In the investigation of specific mechanisms, however, it is suggested that rate data for the specific reactions involved be used whenever possible.

SECTION II

INTRODUCTION

OBJECTIVE AND SCOPE

This report reviews the scientific literature relating to the oxidation of sulfur dioxide in power plant plumes, and provides recommendations on conversion rates to be applied in atmospheric dispersion models, based on current knowledge in this field. The importance of these two objectives derives both from the presently confused state of our knowledge regarding atmospheric SO_2 oxidation processes and from the potentially great problems associated with our rapidly increasing sulfur dioxide emissions.

Recognizing these problems, a program has been initiated to provide a more complete means for evaluation of the atmospheric impact of increased fossil fuel combustion. The first component of this program has been a review of the behavior of plumes emitted from large, elevated (primarily fossil fuel combustion) sources, which has been documented in the report Tall Stacks and the Atmospheric Environment[1]. From this report it is highly evident that our present ability to predict the atmospheric impact of increased fuel utilization is limited by lack of knowledge regarding in-plume SO_2 conversion processes. The present report is intended to help rectify this situation somewhat by providing

a summary of the limited existing knowledge regarding these processes. A third and final report will describe a reactive dispersion model developed for use in conjunction with recommended reaction rate parameters to evaluate the atmospheric impact of power plant plumes, over moderately large scales of time and distance.

CLASSIFICATION OF CHEMICAL REACTIONS -- REPORT ORGANIZAT

The reactions by which SO_2 may be oxidized are generally divided into two groups identified by the terms 'homogeneous' and 'heterogeneous'. Homogeneous reactions are those in which all reactants (including catalysts) are in the same phase (i.e. gas, liquid, solid); heterogeneous reactions involve more than one phase. In the gas phase, SO_2 oxidation reactions may be either homogeneous or, if particulate matter is also present, heterogeneous. In the aqueous phase, the significant oxidation reactions are at least quasi-homogeneous; that is, all the reactants are in solution, even if the aqueous phase consists of a water sheath around an aerosol particle. Thus, the important oxidation reactions to be considered in the atmosphere occur *via* gas phase homogeneous and heterogeneous paths and by aqueous phase homogeneous paths.

In general terms, the title of a review by Urone and Schroeder[2] essentially summarizes the status of our understanding of SO_2

oxidation chemistry: "SO_2 in the Atmosphere: A Wealth of Monitoring Data but Few Reaction Rate Studies". It is of interest that despite numerous studies on both the heterogeneous and homogeneous aspects of SO_2 oxidation, there is no consensus on the predominant path of this reaction in the atmosphere in general, or in plumes in particular. There are more studies supporting the predominance of heterogeneous paths, but some recent studies seem to suggest homogeneous rates greater than two percent per hour, higher than previously observed. In addition, the difficulties inherent in assessing the importance of the various paths, especially the aqueous phase reactions, are compounded by an acute dependence on meteorological factors. In this report, the oxidation of SO_2 is reviewed as follows:

Thermochemistry
Plume studies
Homogeneous studies in the gas phase
Homogeneous studies in the aqueous phase
Heterogeneous studies
Modelling applications.

The Appendix contains a brief review of thermochemical kinetics and definitions of the basic chemical terms which will be used throughout the report. It is included for the sake of completeness and also as an aid for the non-chemist.

The literature concerning various aspects of the oxidation of SO_2 has been reviewed by several authors (Urone and Schroeder

(2), Kellog, *et al.* (3), Cadle (4), M. Bufalini (5), A. P. Altshuller and J. Bufalini (6), Harrison, *et al.* (7), Pierrard (8)). In general, the available literature pertaining to each of the topics to be discussed in this report varies widely in both quantity and quality, making the extraction of relevant data and conclusions difficult. The aim of this review, then, is to extract the data which are available from the literature, however qualified they may be, and also to draw attention to the areas most lacking in substantive conclusions.

SECTION III

THERMOCHEMISTRY OF SO_2 OXIDATION

In the gas phase, the production and subsequent reaction of sulfuric acid (H_2SO_4) in a plume involves the oxidation of SO_2 to SO_3, hydration of SO_3, condensation of the resulting acid, and reactions with particulate matter. Equilibrium constants for the oxidation of SO_2 are presented in Table 1.[9] It becomes apparent

Table 1. Equilibrium Constants for the Reaction $SO_{2(g)} + 1/2\ O_{2(g)} \rightleftarrows SO_{3(g)}$[9].

Temperature °K	Temperature °C	Equilibrium constant ($P_{SO_3} P_{SO_2}^{-1} P_{O_2}^{-1/2}$) $atm^{-1/2}$
300	80	2.069×10^{12}
400	260	1.088×10^{8}
500	440	2.608×10^{5}
600	620	4.892×10^{3}

that, under conditions pertinent to gases leaving the stack (<500 °K) and entering the plume (300-400 °K), the equilibrium so heavily favors the formation of SO_3 that in the absence of kinetic factors, there would essentially be no SO_2 present. These kinetic factors, and the ways in which they influence the oxidation rate, will be addressed in subsequent sections of this report.

Thermodynamically, the hydration of SO_3 to gaseous H_2SO_4 also becomes more favorable as the temperature drops. Figure 1, from Leppard's review[10], shows that at temperatures existing in plumes essentially all the SO_3 is converted to H_2SO_4 under equilibrium conditions. This conversion is also achieved rapidly: dry sulfur trioxide will form an aerosol almost immediately upon contact with moist air.

Thermodynamic values for the dewpoint of gaseous H_2SO_4 have been reviewed by Verhoff and Banchero[11]. Figure 2, again from Leppard, compares calculated and experimental dewpoint curves. The rate of condensation is rapid, even at the concentrations at which SO_3 or H_2SO_4 is emitted from stacks.

The processes involved in the oxidation of SO_2 in the aqueous phase include absorption of SO_2 and other gases, hydration and subsequent dissociation of the dissolved species, and oxidation of sulfite or bisulfite ions. Because these processes are highly dependent on thermodynamic factors, the appropriate equilibria will be discussed later in conjunction with the relevant kinetic factors. In general, however, the oxidation process in the aqueous phase is thermodynamically favored, as it is in the gas phase.

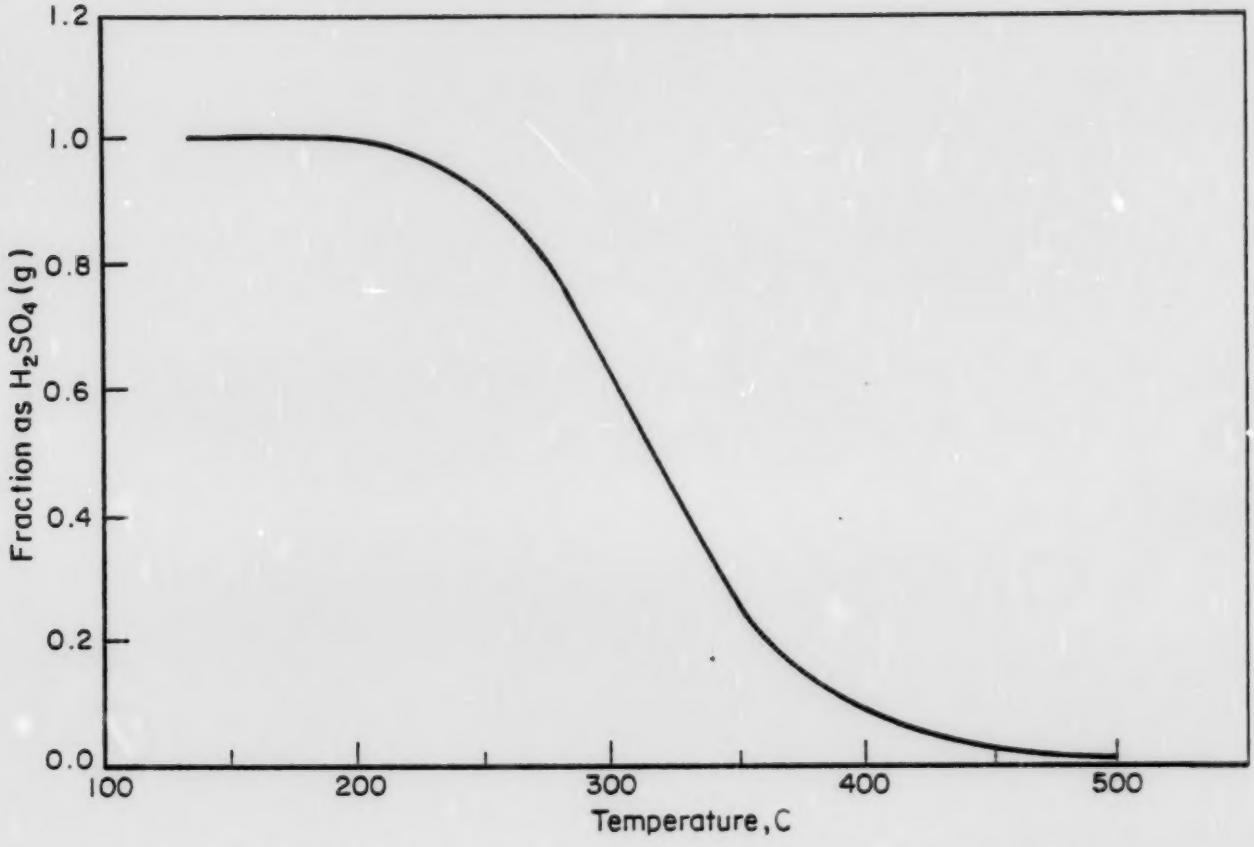


FIGURE 1. EQUILIBRIUM CONVERSION

$SO_3(g) + H_2O(g) == H_2SO_4(g)$ (10)

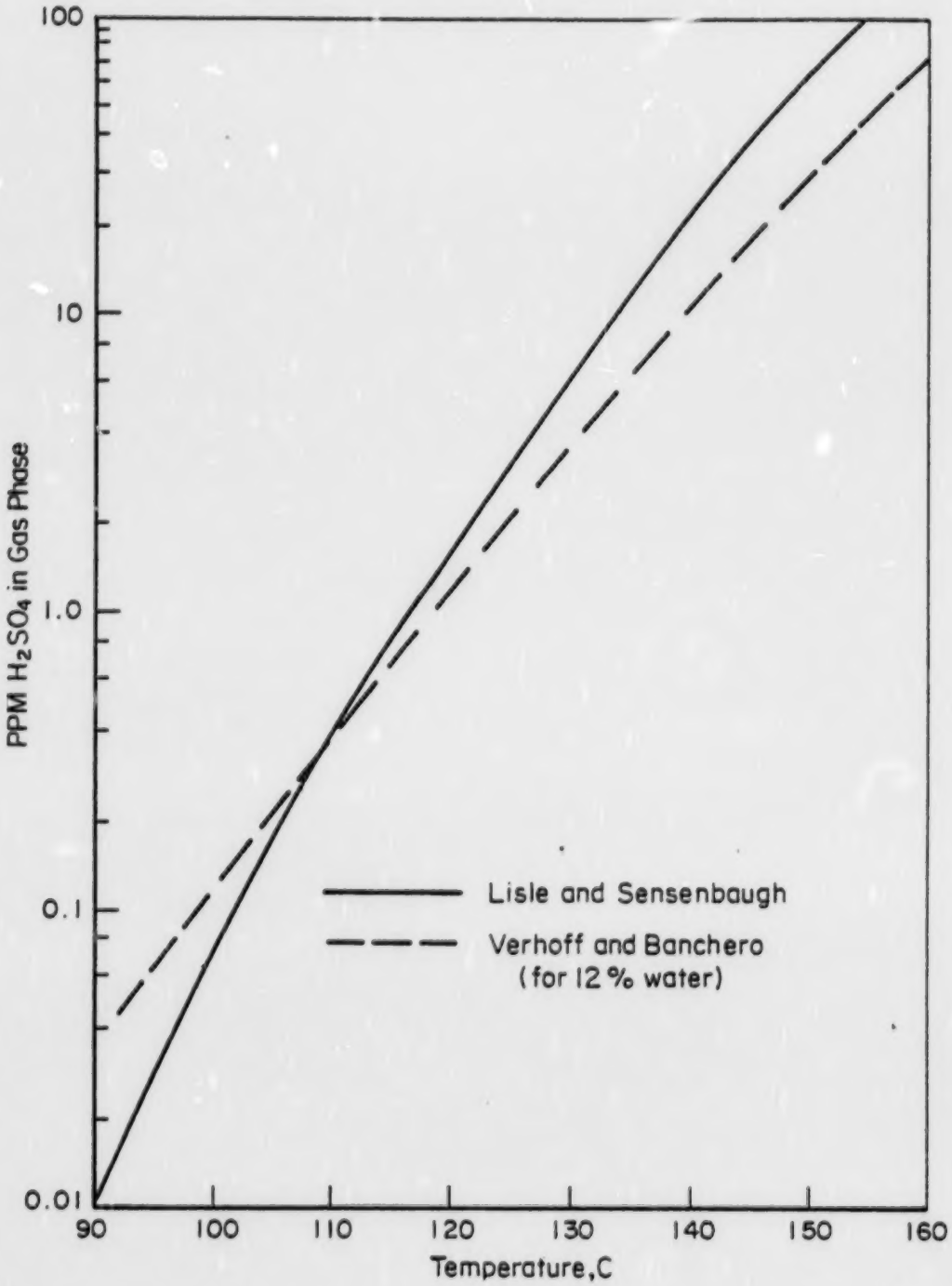


FIGURE 2. DEW POINT OF H_2SO_4(g) [10]

SECTION IV

PLUME STUDIES

From a practical point of view, the most obvious or straightforward way to examine SO_2 oxidations would be to make measurements directly in actual plumes. This approach has been carried out by a number of laboratories, but unfortunately with minimal success. Experimentally it is essentially impossible to control conditions in the plume; added to this is the fact that such measurements are very difficult to carry out. For this reason, results obtained from such studies tend to conflict, making it difficult to draw meaningful conclusions about plumes in general or to even compare the studies to each other. Table 2 presents a summary of the studies performed to date.

One of the first plume studies directed toward examination of SO_2 - sulfate relationship, conducted by Gartrell *et al.*, of the Tennessee Valley Authority (TVA)[12], has become nearly classic, in that investigators often attempt to relate theoretical and laboratory experimental results to the TVA results. The TVA program attempted to measure both SO_2 and SO_3 in the plume; however, the instrumentation of that period (early 1960) was not well suited to making SO_3 (or H_2SO_4) measurements.* Table 3, taken from the

*The inability to make simple, reliable measurements of ambient H_2SO_4 levels remains as possibly the most severe limitation to studies of the fate of SO_2 in plumes today.

Table 2. SUMMARY OF STUDIES OF SO_2 OXIDATION IN ACTUAL PLUMES.

Study	Species Measured	Comments
Gartrell, *et al.* (1963)[12]	SO_2, SO_3	Highly variable oxidation rates. Positive correlation with humidity.
Dennis, *et al.* (1969)[13]	SO_2 relative to SF_6	SO_2 half life from 1.0 to 2.8 hours (mean 1.5 hours).
Coutant, *et al.* (1972)[14]	SO_2	Laboratory simulation, various fuels. SO_2 loss highly dependent on humidity.
Stephens and McCaldin (1971)[15]	SO_2 relative to submicron aerosol	Oxidation rate dependent on humidity.
Weber (1970)[16]	SO_2 relative to CO_2	Increasing oxidation rate with increasing humidity.
Newman, *et al.* (1975)[17,18,19]	^{32}S, ^{34}S	Higher oxidation rates in plumes from oil-fired plants than coal-fired. No specific humidity dependence noted.
University of Utah (1975)[20]	Particulate $(NH_4)_2SO_4$ relative to ambient SO_2	Low oxidation rates, possibly due to low humidity.
Davis and Klauber (1975)[21]	NO, NO_2, O_3, SO_2	Ozone 'bulge' noted downwind.
Whitby, *et al.* (1975)[23]	Aerosol	Results of single flight Oxidation rates of 1.5 - 1.8 %/hr inferred.

TVA study, presents a brief summary of the oxidation rates resulting from measurements made in the plume of the Colbert power plant, near Wilson Dam, Alabama. The results show that in periods of low humidity, SO_2 oxidation was quite low, ranging from 1-3 percent per hour. At high relative humidity, a rate of some 30 percent per hour (55% over 108 minutes) was observed.

Probably the most significant finding coming out of this study was the extreme variability of SO_2 oxidation rates. This variability may have been the result of changing meteorological conditions, the difficulties of analysis, or factors unknown. It is of interest to note that in spite of the tendency of later workers to attempt to relate back to these studies, it was never the intent of the authors to consider this a definitive study - in the words of the authors, "These limited data do not provide a basis for an accurate estimate of the absolute rate of SO_2 oxidation after emission." The fact remains, however, that as the first major study of its kind, this work provided a foundation for subsequent studies by pointing out some of the important variables and giving at least a qualitative idea about the nature of SO_2 - plume chemistry.

TABLE 3. SO_2 OXIDATION STUDIES COLBERT STEAM PLANT PLUME[12]

Date 1960	Sample No.	Travel from Point of Emission: Time (min)	Travel from Point of Emission: Distance (miles)	Relative Humidity in Plume (Percent)	SO_2 Oxidation (Percent)
		"Low Rates"			
8/2	1	5	.25-1		0
	2	5	.25-1		0
	3	5	.25-1		1.20
	4	15	1-1.5		0
9/2	1	30	2-3		3.70
	2	78	8		2.20
10/14	1	12	.5-1.5	62	2.15
	2	60	5-6	54	3.23
10/26	1	6	.25-1.25	45	1.50
	2	84	8-9	48	2.70
10/28	1	12	.5-1.5	68	1.10
	2	84	8-9	70	4.10
		"High Rates"			
5/3	1	13	1.1		13.80
	2	13	1.1		10.00
	3	13	1.1		19.20
8/19	1	108	8-10		55.50
	2	23	.75-2		8.00
10/11	1	12	.5-1.5	74	21.60
	2	96	8	73	32.00

A few years after the TVA study, a study was carried out by Dennis *et al.* of the GCA Corporation[13], in which SO_2 losses in stack plumes were determined downwind from a 330-MW coal-fired power plant. Since it was not feasible to measure SO_2 directly, SO_2 losses were determined relative to SF_6, a commonly-used non-reactive tracer. The results of this program were inconclusive. The half-life of SO_2 under the field conditions ranged from 1.0 to 2.8 hours with a mean value of 1.5 hours. There were some discrepencies in this study in extrapolating the field SO_2/SF_6 ratios back to the expected source value for this ratio: Some extrapolations suggested fairly rapid half-lives, such as 0.13 hours. Relative humidities in this program ranged from 36-53 percent.

As a follow-up to this study a laboratory program was carried out by Coutant *et al.*, at Battelle-Columbus Laboratories primarily focused on determining if SO_2 decay was as rapid as the GCA data suggested within a half mile of the power plant[14]. In this program, a time-temperature simulation of the stack gases leaving the furnace was established. The burner was fueled with three types of coal (at 30 lb/hr) and two oils (at 3 gal/hr) to assess the variation of the SO_2 oxidation rate with fuel composition. When burning coal, there was about a 10 percent loss of SO_2 in the flue gas within the boiler-economizer section, while there was essentially no loss of SO_2 when burning oil. In the plume region, loss of SO_2 was very dependent on humidity. First-

order rate constants for the loss of SO_2 varied from 2×10^{-3} to 13×10^{-3} min^{-1} ($t_{1/2}$ of 1-6 hours).

Stephens and McCaldin[15] carried out a series of measurements in a power plant plume by assuming that particulate matter in the submicron size range constitutes a conservative (non-varying) tracer, and relating SO_2 measurements to this quantity. Friend[22] has taken exception to such a procedure on the grounds that SO_2 can be oxidized to sulfate in particulate form, thus invalidating the assumption that particulate matter is a conservative tracer. This point notwithstanding, Figure 3 (taken from their study) gives some appreciation of the nature of the results. Half-lives for curves A, B, and C are:

Curve	RH	$t_{1/2}$
A	30 - 40%	--
B	40 - 55%	144 min
C	78 - 80%	70 min

The results support the generally established concept that humidity exerts a major influence in the oxidation of SO_2 in the atmosphere.

Weber[16] has made measurements of SO_2 decay using CO_2 as his conservative tracer. His measurements were not made in an elevated plume, but at ground-level sampling sites downwind of a power plant. Using calculated CO_2/SO_2 ratios for the effluent

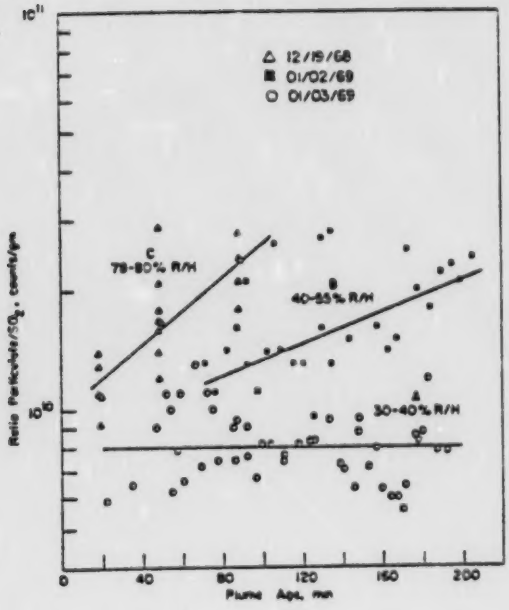


FIGURE 3. SULFUR DIXOIDE DECAY RATES IN THREE RELATIVE HUMIDITY RANGES (15)

leaving the stack of a power plant in Frankfurt am Main, he then observed CO_2/SO_2 ratios at various distances from the plant. His results only allow for generalized statements on rates of oxidation. He reports rather short half-lives (20 minutes to 1 hour) depending on meteorological conditions (which are not well-defined). He also reports an increase in $\Delta CO_2/\Delta SO_2$ with increasing relative humidity, indicative of an increasing oxidation rate (here, Δ indicates the difference between the peak and background levels).

The Brookhaven National Laboratory (BNL) has been carrying out fairly extensive studies of SO_2 oxidation in plumes of oil[17] and coal-fired[18] power plants. The BNL studies were carried out with the aid of single engine aircraft outfitted with a high volume sampler for collecting and measuring sulfate and with SO_2 absorption scrubbers for applying the BNL isotopic ratio technique[19]. The particulate sulfate catches were too small to be adequate for accurate analysis. The isotopic ratio technique depends on measuring the changes in the ratio of the two most abundant isotopes of sulfur, $^{32}S/^{34}S$. Since the technique measures the sulfur originating with the fuel, it can theoretically discriminate between sources, and thus lends itself to the study of a specific source.

Small deviations from standard isotopic sulfur ratios are expressed by a 'del value':

$$\delta S = \left[\frac{^{32}S/^{34}S \text{ (standard)}}{^{32}S/^{34}S \text{ (sample)}} - 1\right] \times 1000 \quad .$$

If isotopic equilibrium is attained between SO_2 and SO_3 so that

$$^{34}SO_2 + {}^{32}SO_3 \overset{K}{\rightleftharpoons} {}^{32}SO_2 + {}^{34}SO_3 \quad ,$$

the equilibrium constant can be written in terms of δSO_2 and δSO_3:

$$K = \frac{1000 + \delta SO_3}{1000 + \delta SO_2} \quad .$$

The fraction of SO_2 converted to SO_3, 1-f, is calculated from the expression

$$\delta SO_2 = \delta SO_2(\text{fuel}) - \alpha(1-f)1000 \quad ,$$

where $\alpha = K-1$. This equation is derived from the definition of K by considering the complete combustion of sulfur in the fuel and an isotopic material balance.

Surprisingly, the oxidation rate in the plumes of the oil-fired plant was higher than that in the coal-fired plant:

oil-fired	$t_{1/2}$ = 10 hours
coal-fired	~ 0% loss.

Newman *et al.* explained that the low oxidation rate in the coal-fired plume was limited by the low particulate content of the plume, where loadings were of the order 10^5 $\mu g/m^3$. No loadings were reported for the oil-fired plumes.

The authors speculate that a catalytic mechanism may be the dominant pathway for oxidizing SO_2 in plumes and refer to indigenous vanadium as a potential catalyst. This conjecture is not to be discounted, but in the same vein, one might also expect sufficient Fe_2O_3 in the particulate matter from the coal-fired plant to catalyze the oxidation of SO_2, and there is growing doubt concerning the catalytic efficiency of vanadium in plumes. (The reader is referred to the section on heterogeneous oxidation of SO_2 for other comments on vanadium catalysis.)

The BNL investigators attempted to fit the decay to first and second order kinetics, and based on a second order mechanism arrive at a rate constant of 1 ppm^{-1} hr^{-1}, which accounts for the 10 hour half-life referred to earlier. No specific dependence on humidity was noted in this analysis, although the RH levels varied from 40-95 percent. In fitting their data to a second order mechanism the authors do not mean to suggest that the oxidation process arises from a bimolecular reaction of SO_2, but that the process involves the reaction of SO_2 with active particles in the plume through water associated with these particles. It is their opinion that any homogeneous mechanism is inconsistent with the isotope ratio data.

A study carried out by the University of Utah Research Institute[20] at the Four Corners power plant in New Mexico in 1974, also provides evidence for low SO_2 oxidation rates in coal-fired power plant plumes. This study was part of an on-going

three-year program to measure the degree of conversion of SO_2 and to evaluate its impact on atmospheric sulfate concentrations and visibility. SO_2 conversion rates were obtained by determining the difference between upwind and downwind concentrations of particulate ammonium sulfate relative to ambient SO_2 and wind speed. Measurements in these tests were made 13 and 37 miles downwind from the plant. Conversions of SO_2 to particulate sulfate were as follows:

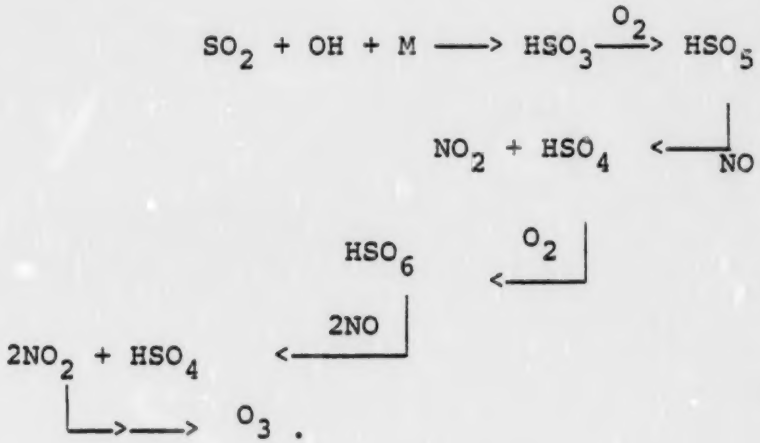
Test 1	0.37%/hr	13 miles downwind	RH 36-51 percent
Test 2	0.76%/hr	13 miles downwind	RH 26-40 percent
	0.45%/hr	37 miles downwind.	

SO_2 concentrations ranged from 0.01-0.06 ppm in these tests.

These results are of interest for several reasons. They are substantially lower than the oxidation rates reported by TVA, possibly because of the low relative humidity at the Four Corners location. Of greater significance, the resultant SO_2 oxidation rates are derived from direct, positive analysis of sulfates and not inferred from the loss of SO_2 relative to some intrinsic tracer in the plume. It is quite possible that in this respect the Four Corners tests provide a more accurate assessment of SO_2 oxidation rates in plumes.

A recent study by Davis and Klauber[21] is cited here, not so much for what it adds to our knowledge on SO_2

oxidation rates, but because it introduces rather different thoughts on the interaction of SO_2 in plumes. They collected extensive data on NO, NO_2, and O_3 and less extensive data on SO_2 in the plume of a 1000-MW power plant firing a mixture of oil and coal. The significant observation in this study was the "ozone bulge" depicted in Figure 4. In these profiles the plume boundaries are well characterized by the drop in the ozone concentration. This is readily accounted for by the rapid reaction between NO and O_3 ($NO + O_3 \rightarrow NO_2 + O_2$). At 50 km downwind, however, one observes an increase in ozone (the "bulge") coincident with low levels of SO_2 measured as "plume SO_2". The authors suggest a series of rather questionable reaction steps to explain the bulge. Of interest to this review, however, is the fact that these reaction steps, if correct, would probably lead to H_2SO_4 and aerosol products which would have some bearing on the rate of oxidation in the atmosphere. The general reaction sequence suggested in this work is:



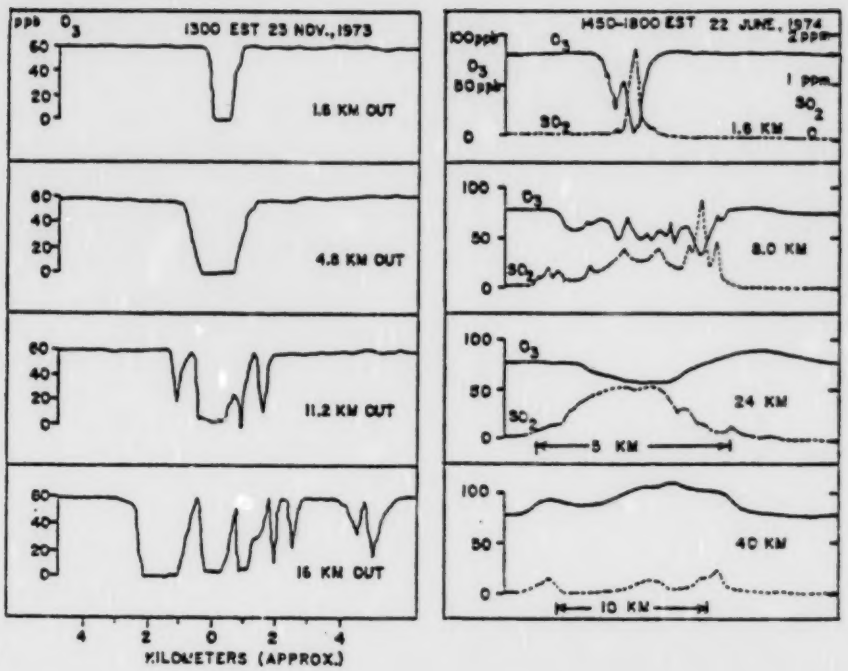


FIGURE 4. CROSSPLUME O_3 AND SO_2 VARIATIONS FOR VARIOUS DOWNWIND DISTANCES(21)

These experiments are reported here with no further comment. Some other work by this group is discussed in the section on homogeneous gas-phase reactions.

Whitby *et al.*[23] conducted sampling flights through the plume of a large power plant near St. Louis, Missouri, as part of the Environmental Protection Agency's Project MISTT (Midwest Interstate Sulfur Transport and Transformation). Using the data from one particularly good run in 1974, they estimate SO_2 conversion rates of 1.5%/hr between 10 and 21 km, and 1.8%/hr between 21 and 32 km downwind. The relative humidity was 75% and the sulfur flow appeared to be constant at 4.08 kg/sec.

Roberts and Friedlander[24] have recently carried out some calculations which permit estimates of gas-to-particle conversion rates for sulfur in trajectories in the Los Angeles basin. These analyses are not based specifically on power plant plume trajectories, but do provide interesting results of pertinence to the oxidation of sulfur dioxide. The authors used total filter and cascade impactor aerosol samples from several sites in the Los Angeles basin. Depending on source and wind direction, SO_2/Total S ratios ranged from 0.88 to 0.98. Estimates of pseudo-first-order rate constants, which appear to be rather high, are presented in Table 4. The accuracy of these data, like all data of this type, is strongly dependent on the method of calculation, the measurement technique, and such complex mechanistic parameters as ozone, free radicals, and humidity.

Table 4. Pseudo First-Order Rate Constants for the Reaction $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ in the Los Angeles Basin (24).

Date (1973)	Time of arrival at Pasadena (PST)	k, %/hr	Starting location
July 10	1300	1.2	El Segundo
	1400	3.0	" "
	1500	9.0	" "
	1600	13.0	" "
July 25	1400	12.8	Alamitos Bay
	1500	8.2	El Segundo
	1600	8.8	" "
July 26	1200	4.3	Alamitos Bay
	1300	5.6	" "
	1400	7.6	" "
	1500	4.7	" "

Table 5 summarizes some of the SO_2 oxidation rates and SO_2 half-lives reported for measurements made in plumes. The data are presented in this table in chronological order of publication. It is interesting to note in this report the general "slowing down" of SO_2 oxidation rates in more recent studies. The significance of this observation is not clear, but it may be indicative of the better, or more reliable, experiments that can be carried out with today's equipment. In essence however, truly reliable estimates for SO_2 oxidation rates in plumes are still wanting. None of the data reported to date can be used without qualification, although this is not meant to fault any of the studies. Primarily the results show the difficulty of such

TABLE 5. SUMMARY OF SO_2 OXIDATION RATES IN PLUMES

	SO_2 Oxidation %/hr	$t_{1/2}$, hrs	R.H., %	Reference
Gartrell *et al.*	0-4	--	45-70	12(1963)
	8-55	--	73	12(1963)
Dennis *et al.*	--	1.0-2.8	36-53	13(1969)
Weber	--	0.3-1	--	16(1970)
Stephens and McCaldin		1.2-2.4	40-80	15(1971)
	0	--	< 35	
Coutant *et al.*	--	1-6	40-90	14(1972)
University of Utah	0.37-0.76	--	26-50	20(1975)
Newman *et al.*	0	--	--	18(1975)
Newman *et al.*	--	10	--	17(1975)
Whitby *et al.*	1.5-1.8	--	--	23(1976)

studies and the need for considerably more data. The increase of SO_2 oxidation rate with increasing relative humidity is fairly well accepted; on the other hand, the results do not provide overwhelming support of this conclusion. Similarly, the dependence of SO_2 oxidation rates on heterogeneous catalysis is accepted by many, yet none of the plume experiments has attempted to link these variables. In summary then, one can only say at this point that SO_2 oxidation rates in plumes may vary from essentially zero to the order of 50 percent per hour. A clearer description of actual SO_2 oxidation processes in plumes will have to await considerably more experimentation.

SECTION V

HOMOGENEOUS STUDIES IN THE GAS PHASE

Until rather recently it was generally felt that SO_2 must be oxidized by heterogeneous (catalytic) paths and that the contribution of homogeneous gas phase reactions was minimal at best. Subsequently, however, there has been reason to challenge this assumption. Although one cannot by any means downplay the potential role of heterogeneous catalysis in SO_2 oxidation, several recent studies of SO_2 oxidation in power plant plumes, cited in the previous section, show lower rates of oxidation than were first reported --- rates well below two percent per hour. It is quite possible that rates of SO_2 oxidation derived from earlier studies were too high because of filter media effects and the poor analytical techniques available (problems which persist to this day) as well as the indirect determination of sulfate formation. Thus, as the reported heterogeneous rates get lower, the homogeneous reaction paths increase in relative importance. This trend has approached the point, in fact, that some investigators argue that homogeneous reaction paths may be at least as significant as heterogeneous paths. It is not our objective to argue this point here; the primary point is that homogeneous reaction rates cannot be arbitrarily assumed to be negligible compared to heterogeneous rates.

Homogeneous gas phase oxidations proceed *via* second or third order processes between SO_2 and molecular or free radical oxidizing agents. Table 6 presents a compilation of homogeneous reaction paths drawn up by Calvert[25]. Although the merits of some of these reaction steps may be questionable, they do show that significant reaction rates can be expected from homogeneous reactions in a plume. The compilation is of special interest in that it offers potential support for rates of 1.7-4.7 percent per hour.

Since the publication of this compilation, Castleman and the group at Brookhaven[26] have examined the reaction $SO_2 + OH \rightarrow HOSO_2^{\cdot}$ in some detail. They report a rate constant of 6×10^{-13} cm^3 $molec^{-1}$ sec^{-1} (887 ppm^{-1} min^{-1}) for this reaction. If the OH radical concentration is 10^7 molecules/cm^3, SO_2 conversion rates of 2 percent per hour would be possible. This conversion rate is of course very dependent upon the OH concentration in the plume: if the assumed OH concentration is an order of magnitude too high (a possibility) then the rate of ~0.23 percent per hour reported in Table 6 would agree with the Castlemen rate data.*

In the Castleman study, the reaction $SO_3 + H_2O + M \rightarrow H_2SO_4 + M$ is

*A basic dilemma that will become apparent in the following discussion is the reliability of the rate data relative to the concentration data of radical species in the atmosphere. Obviously this dilemma becomes even more severe in chimney plumes where the concentrations of radical species are even more in doubt.

TABLE 6. ESTIMATED RATES OF THEORETICALLY POSSIBLE HOMOGENEOUS REMOVAL PATHS FOR SO_2 IN A SIMULATED POLLUTED ATMOSPHERE[267]

	ΔH_{298}, kcal/mole	Approximate Rate, % per hr
$SO_2 + 1/2\ O_2 + \text{Sunlight} \rightarrow SO_3$	-24	< 0.021
$O(^3P) + SO_2 + \underline{M} \rightarrow SO_3 + \underline{M}$	-83	0.014
$O_3 + SO_2 \rightarrow SO_3 + O_2$	-56	0.00
$NO_2 + SO_2 \rightarrow SO_3 + NO$	-10	0.00
$NO_3 + SO_2 \rightarrow SO_3 + NO_2$	-33	0.00
$N_2O_5 + SO_2 \rightarrow SO_3 + N_2O_4$	-24	0.00
$CH_2(O_3)CH_2 + SO_2 \rightarrow SO_3 + 2CH_2O$	-81	< 0.4-3.0
$\cdot CH_2OO \cdot + SO_2 \rightarrow SO_3 + CH_2O$	~ -117	< 0.4-3.0
$CH_2{=}O{-}O + SO_2 \rightarrow SO_3 + CH_2O$	~ -85	
$HO_2 + SO_2 \rightarrow HO + SO_3$	-19	0.85
$\rightarrow HO_2SO_2^{\cdot}$	< -25	?
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$	-30	~ 0.16
$\rightarrow CH_3O_2SO_2^{\cdot}$	< -25	?
$HO + SO_2 \rightarrow HOSO_2^{\cdot}$	~ -82	~ 0.23
$CH_3O + SO_2 \rightarrow CH_3OSO_2^{\cdot}$	~ -73	~0.48

Total potential rate of conversion of SO_2 to SO_3 (or Sulfates) $\cong$ 1.7-4.7% per hour.

also examined.* Using fast-flow reaction techniques the pseudo-bimolecular rate for homogeneous reaction was found to be 9.1 x 10^{-13} cm^3 $molec^{-1}$ sec^{-1}; the actual termolecular reaction rate at 1.3 Torr and 300°K is thus 2.2 x 10^{-29} cm^6 $molec^{-2}$ sec^{-1}. (The proportionality factor between the two values is, of course, [M] at the experimental temperature and pressure.) Assuming a four-center intermediate complex for the formation of H_2SO_4, this appears to be a very rapid rate.

One of the basic questions in assessing the homogeneous rate of SO_2 oxidation in the atmosphere is how fast the reaction can proceed in a clean air system. Gerhard and Johnstone[27], in their early work in this area, reported an oxidation rate of 0.1 percent per hour in natural sunlight and rates of the order of 0.68 percent per hour in U.V.-irradiated systems (2950-3650 Å) with NO_2.

Calvert's group[28] considered the photooxidation reaction from basic principles. Based on new estimates for the triplet SO_2 quenching rate with N_2, O_2, H_2O, Ar, He and NO this group estimates that the maximum rate for the homogeneous oxidation is 1.9 percent per hour. Friend[29] disagrees with this estimate, believ-

*The intermediate of a reaction is a state in which the two reactants are bound in an energetic, short-lived complex. In many cases, the intermediate is so highly energetic that it flies apart before the rearrangements necessary for the formation of products can be accomplished. However, if a third body (molecule or atom) collides with the complex, it can draw off some of the energy, giving the complex a longer lifetime and greatly increasing the chance of formation of products; the reaction is then termolecular, and the third body is designated M. In the atmosphere, of course, M is generally N_2 or O_2.

ing that assumed quantum yields for SO_2 removal of 0.01-0.001 are much too high, and are actually closer to 10^{-9}. On this basis, Friend would estimate the homogeneous rate of oxidation to be near zero.

A number of investigators have considered the oxidation of SO_2 and subsequent particle formation in the presence of NO_2. The most pertinent considerations are those of Cox[30] and Jaffee and Klein[31]. Cox considers the oxidation of SO_2 and of NO_2 and their roles in the heteromolecular condensation of H_2SO_4 aerosols. Using HO_2 as a possible free radical intermediate, the highest SO_2 conversion rate one might expect from his data is 0.1%/hr. This estimate is based on the reaction

$$SO_2 + HO_2 \overset{k}{\rightarrow} SO_3 + HO \quad ,$$

where $k = 3 \times 10^{-16}$ cm^3 $molecule^{-1}$ sec^{-1} and the HO_2 and SO_2 concentrations are 5×10^8 molecules/cm^3 and 30 ppb respectively. Cox's analysis shows that the rate of formation of H_2SO_4 in urban air is sufficient for hetermolecular nucleation to form aqueous sulfuric acid aerosols, while in background areas SO_2 oxidation products are removed mainly by condensation on existing aerosol.

Jaffee and Klein irradiated NO_2 in the presence of SO_2 at 3660 Å, a wavelength at which SO_2 is not excited, but NO_2 is photolyzed to NO and O. The rate constant for the reaction $SO_2 + O \overset{k_1}{\rightarrow} SO_3^*$ is reported to be 1.1×10^9 ℓ $mole^{-1}$ sec^{-1}. When combined with the

deactivation processes $SO_3^* \xrightarrow{k_2} O + SO_2$ and $SO_3^* + M \xrightarrow{k_3} SO_3 + M$, the rate constant k_4 for overall reaction $SO_2 + O + M \xrightarrow{k_4} SO_3 + M$ is given by the expression

$$k_4 = k_1 / (k_2/k_3 + M) \quad .$$

(The intermediate SO_3^* is assumed to be at its steady state concentration.) The ratio k_2/k_3 was found to be 0.077 mole ℓ^{-1}, making $k_4 = 1.4 \times 10^{10}\ \ell^2\ \text{mole}^{-2}\ \text{sec}^{-1}$ under the experimental conditions where $[M] \simeq 10^{-4}$ mole ℓ^{-1} (2 Torr). At atmospheric pressure, M makes only a slightly more significant contribution (assuming the mechanism is still valid), leading to a value of $k_4 = 9.3 \times 10^9\ \ell^2\ \text{mole}^{-2}\ \text{sec}^{-1}$. If we assume some 10^4 oxygen atoms/cm^3 in a plume, the half-life for the reaction is 1.1×10^8 sec (3.5 years), implying that the process is negligibly slow.

Direct oxidation of SO_2 by ozone in the gas phase is also a slow process. In a power plant plume the process is probably of even less importance because of the rapid removal of ozone by the NO in the plume. Cox and Penkett[32] have considered the oxidation of SO_2 in a system containing olefin and ozone. They postulate that the SO_2 reacts with an intermediate product (I) resulting from the reaction between ozone and olefin. The rate of SO_3 formation is then expressed by $R_{SO_3} = k(SO_2)(I)$. The consequences of these reactions may be greater in terms of long-range SO_2 transport than in short-term plume chemistry due to the aforementioned rapid reaction between O_3 and NO.

Smith and Urone[33] have performed studies of the photochemical oxidation of SO_2 alone and in the presence of NO_2, propylene (C_3H_6), and water vapor. The initial SO_2 concentration throughout the study was 2 ppm. In air containing only SO_2, the initial photochemical rate (dSO_2/dt) was 1.74×10^{-4} ppm/min (about 0.55%/hr). The introduction of NO_2 increased this rate when the SO_2:NO_2 ratio was 1 or 2, but decreased it when the ratio was 0.6 or less. When both NO_2 and propylene were added, the rate increased by some two orders of magnitude over the rate for the SO_2-air system, and was found to be a function of both the propylene and NO_2 concentrations. The addition of water vapor at 50% relative humidity to the SO_2 - NO_2 system was found to increase the rate about tenfold over that for the dry system, but for unknown reasons a similar addition to the SO_2 - NO_2 - propylene system had no effect.

Wilson and Levy[34,35] have also examined the smog process in irradiated SO_2 - NO - hydrocarbon systems. This work was directed at observing the effects of SO_2 in smog rather than the reverse. It was generally observed in this work, however, that the decay of SO_2 increased in proportion to the reactivity of the hydrocarbons. No quantitative values came out of these studies.

In a current program under EPA-sponsorship, D. F. Miller[36] is studying the homogeneous rate of oxidation of SO_2 in photochemical smog systems. The studies are being conducted in a large 610-cu-ft smog chamber, and while there are admittedly certain

limitations to such a device as a basic kinetic tool, a definite influence of hydrocarbon concentration is being observed in these studies. Rates of SO_2 oxidation, which appear to be homogeneous and not especially influenced by the chamber walls, are of the order of 2-6 percent per hour. Increasing the propylene from 1.6 ppm (as carbon) to about 3 ppm doubled the homogeneous rate.

Roberts and Friedlander[37] have recently carried out experiments designed to study the formation of sulfur-containing aerosols under ambient photochemical smog conditions. These experiments were carried out in a large (96 m^3) Teflon chamber irradiated with natural sunlight. Seven olefins were used in these studies, although most of the experiments dealt with 1-heptene-SO_2-NO systems. Based on pseudo-first order depletion of SO_2, the reaction rates varied from 0-90 percent per hour, depending on the initial SO_2 level. The relative humidity was quite low (< 40%), making the extremely high rates even more surprising, although no explanation of the high rates was offered. The authors do develop some theoretical kinetic analyses using a mechanism similar to that of Cox and Peckett (discussed earlier) and present an expression for estimating aerosol sulfur content. The experimental results appear consistent with a mechanism for the formation of the ozone-olefin intermediate (I).

Davis[21] has also reviewed some aspects of homogeneous SO_2 oxidation kinetics with a slightly different approach from that of Calvert. Davis considers the following processes and estimates SO_2 lifetimes* for the lower troposphere as shown in Table 7:

(1a) $SO_2 + h\upsilon(2400\text{-}3400\ \mathring{A}) \rightarrow SO_2^*$

(1b) $SO_2^* + O_2 \rightarrow (SO_4)$

(2) $SO_2 + O + M \rightarrow SO_3 + M$

(3) $SO_2 + O_2(^1\Delta) \rightarrow (SO_4)$

(4) $SO_2 + O_3 \rightarrow SO_3 + O_2$

(5) $SO_2 + NO_3 \rightarrow SO_3 + NO_2$

(6) $SO_2 + N_2O_5 \rightarrow SO_3 + N_2O_4$

(7) $SO_2 + HO_2 \rightarrow SO_3 + OH$

(8) $SO_2 + OH + M \rightarrow HSO_3 + M$

(9) $SO_2 + CH_3O_2 \rightarrow SO_3 + CH_3O$

Reaction 8 is the most probable for the homogeneous oxidation of SO_2 in the atmosphere. Thus, the structure and reactions of the product of reaction 8, HSO_3, is very critical to acid aerosol formation in the atmosphere. It is on this basis that Davis puts forth the extensive series of reactions on the oxidation of HSO_3 discussed in the section on plume studies.

*The term "lifetimes" is frequently seen in the literature, and is equivalent to "half-life".

Table 7. SO_2 LIFETIMES FOR CONVERSION TO H_2SO_4 IN TROPOSPHERE[21]

Reaction	Second Species	Concentration Molecules/cm^3	Lifetime days
1	--	--	4×10^7
2	O (^3P)	$\sim 1 \times 10^4$	$\sim 6 \times 10^4$
3	O_2 ($^1\Delta$)	$\sim 10^6$	$\sim 10^8$
4	O_3	1×10^{12}	$\sim 10^5$
5	NO_3	$\sim 1 \times 10^7$	$\sim 10^{16}$
6	N_2O_5	$\sim 6 \times 10^6$	$\sim 10^9$
7	HO_2	$\sim 5 \times 10^8$	~ 23
8	OH	$\sim 5 \times 10^6$	~ 3
9	CH_3O_2	$\sim 10^8$	100

Some of the reactions presented in this discussion are summarized in Table 8. It becomes very apparent when one considers the role of homogeneous removal paths for SO_2 that, although the specific rate data are possibly good only within a factor of 10, this uncertainty may not be the most serious problem to assessing the role of homogeneous reaction paths. The various concentrations of radical species presented in Tables 7 and 8 are not well established for conditions in the troposphere, and the existing data concerning them may be even less reliable for conditions in a power plant plume.

One might summarize this section with the conclusion that homogeneous SO_2 oxidation reactions can play a significant role in atmospheric reactions under certain meteorological conditions, but one must still question the significance of these reactions in the power plant plume. At any rate, it is fairly obvious that we are not confident of just how to apply homogeneous reaction steps to mechanisms concerning the oxidation of SO_2 in plumes.

TABLE 8. ESTIMATED RATES OF SO_2 REMOVAL

T ≅ 300 K

	Rate Constant k, cm^3 $molecule^{-1}sec^{-1}$	Rate (approximate), Percent per hour	Remarks	Reference
$SO_2 + 1/2\ O_2 = SO_3$	2.9×10^{-26}	0.05		38
	5.7×10^{-28}	0.001		33
$SO_2 + O_2\ (^1\Delta g) = SO_3 + O$	3×10^{-16}	0.01	$[O_2(^1\Delta g)] = 10^8 cm^{-3}$	39
$SO_2 + O\ (+M) = SO_3\ (+M)$	1.9×10^{-13} *	0.007	$[O(^3P)] = 5 \times 10^5\ cm^{-3}$	40
	1.8×10^{-12}	.001	$[O(^1D)] = 5 \times 10^3\ cm^{-3}$	31
	3.2×10^{-13} *	0**	"	
	1.2×10^{-14} *	0	"	
	1.9×10^{-14} *	0	"	
$SO_2 + HO\ (+M) = HSO_3\ (+M)$	$(3.8\text{-}5.2) \times 10^{-13}$	1.6	$[HO] = 10^7\ cm^{-3}$	26
	1.1×10^{-12}	3.9	"	21
	2.5×10^{-12}	8.9	"	7
	3.7×10^{-12}	13.3	"	41
$SO_2 + HO_2 = SO_3 + HO$	9×10^{-15}	1.6	$[HO_2] = 5 \times 10^8\ cm^{-3}$	41
	3×10^{-16}	0.05	"	28
	9×10^{-16}	0.16	"	21
$SO_2 + O_3(+H_2O) = SO_3 + O_2\ (+H_2O$	2.8×10^{-17}	25.	$[O_3] = 2.5 \times 10^{12}\ cm^{-3}$, pH = 6	42
	2.8×10^{-19}	0.25	, pH = 4	42
$SO_2 + NO_2 = SO_3 + NO$	6.1×10^{-24}	0	$[NO_2] = 1.2 \times 10^{12}\ cm^{-3}$	31
	$< 2 \times 10^{-24}$	0		21
	4.9×10^{-31}	0	k extrapolated from 700 K to 300 K	21
$SO_2 + H\ (+M) = HSO_2\ (+M)$	3.5×10^{-14} *	0	[H] est. $10^5\ cm^{-3}$	44

* Termolecular constant expressed as second order, $M = 2.5 \times 10^{19}\ cm^{-3}$.

** 0 rates < 0.001%/hr.

SECTION VI

HOMOGENEOUS STUDIES IN THE AQUEOUS PHASE

A consideration of primary importance to the question of aqueous-phase SO_2 oxidation is the dissociation behavior of this material in water. The fact that SO_2 does form a hydrate which dissociates in water to yield an acidic solution has been recognized for many years, but until relatively recently the rate of this dissociation process and its products have been open to speculation. A great many authors, for instance, have presumed that undissociated sulfurous acid, H_2SO_3, is formed upon dissolution of SO_2 in water. Spectroscopic studies[45], however, indicate that, while H_2SO_3 does not exist to any appreciable extent in the SO_2-H_2O system, such species as undissociated SO_2, HSO_3^-, $SO_3^=$, pyrosulfite ions (eg. $HS_2O_5^-$), and hydrates ($SO_2 \cdot nH_2O$) do exist in measurable quantities. Furthermore, SO_2, HSO_3^-, and $SO_3^=$ are the most abundant species, and for most practical applications one can represent the dissociation process in terms of the equations

$$SO_{2(g)} \overset{K_0}{\rightleftharpoons} SO_{2(aq)} \qquad (1)$$

$$SO_{2(aq)} + H_2O \overset{K_1}{\rightleftharpoons} HSO_3^- + H^+ \qquad (2)$$

$$HSO_3^- \overset{K_2}{\rightleftharpoons} SO_3^= + H^+ \quad . \qquad (3)$$

Here the K's denote equilibrium constants defined by the following expressions:

$$K_0 = \frac{[SO_2]}{P_{SO_2}}$$

$$K_1 = \frac{[HSO_3^-][H^+]}{[SO_2]}$$

$$K_2 = \frac{[SO_3^=][H^+]}{[HSO_3^-]}$$

Values of the equilibrium constants have been measured experimentally, and are given as functions of temperature in Table 9. These values can be utilized in conjunction with the above equations to demonstrate that, under typical environmental conditions, the preponderance of sulfur dioxide dissolved in water exists in the form of HSO_3^- ions.

The question of the rates of the dissociative processes (2) and (3) has also been debated actively up until the very recent past. Early semi-quantitative measurements indicating these reactions to be extremely rapid were questioned in the subsequent chemical engineering literature, and the quantitative results of Wang and Himmelblau[46] implied that the ionization processes were sufficiently slow to be rate influencing under a number of circumstances.

Wang and Himmelblau were apparently unaware, however, that Eigen *et al.*[47] had performed a previous definitive measurement of the rates of ionization of hydrated SO_2, which strongly indicates their later results to be in error. Eigen's measurements indicate that ionization approaches completion at times of the order of 10^{-5} seconds, thus enabling these reactions to be regarded as essentially instantaneous for this assessment of oxidation processes.

TABLE 9. TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS FOR THE SO_2-H_2O SYSTEM[48]

Temperature	K_0	K_1	K_2
25°C	1.24 M atm^{-1}	.0174 M	6.3×10^{-8} M
15	1.83	.0219	7.9×10^{-8}
10	2.25	.0247	8.9×10^{-8}
0	3.46	.0319	11.4×10^{-8}
-3	3.97	.0346	12.4×10^{-8}

The literature pertaining to the aqueous phase homogeneous oxidation of SO_2 is in some ways more pleasing than that for the gas phase (a summary is given in Table 10). For instance, there is general agreement that in the aqueous phase, the oxidation of S(IV) by O_2 must be catalyzed in order to proceed at an appreciable rate, and almost without exception the suggested catalyst has

TABLE 10. SUMMARY OF AQUEOUS PHASE SO_2 OXIDATION MECHANISMS

AUTHOR	TYPE OF MECHANISM	ELEMENTS OF MECHANISM	RATE COEFFICIENTS AND/OR EXPRESSIONS	COMMENTS
Fuller and Crist 1941 (49)	Sulfite oxidation by O_2 with no catalyst; Cu^{2+} catalyst; mannitol inhibitor	very long chain reaction	$\frac{d(O_2)}{dt} = k(SO_3^{--})$ $k = .013 + 2.5(Cu^{2+})$ with cu^{2+} catalyst; $k = .013 + 6.6\ (H^+)^{1/2}$ with acid added	25°C; rate coefficient with acid added assumes second dissociation of H_2SO_3 equals 5×10^{-6} (too large)
Bassett and Parker 1941 (50)	Sulfurous acid oxidation by metal salts and O_2	uncatalyzed: formation of complexes such as $[O_2 \cdot SO_3]^{--}$; catalyzed: formation of complexes such as $[O_2 \cdot Mn(SO_3)_2]^{--}$ and rapid oxidation		
Junge and Ryan 1958 (51)	SO_2 oxidation catalyzed by Fe^{2+}, with and without ammonia		conversion rate $= 1.8 \times 10^{-4}$ %/min	sulfate formation asymptotic to a certain pH; maximum formation varies linearly with SO_2 partial pressure
Van den Heuvel and Mason 1962 (52)	SO_2 oxidation catalyzed by NH_3	$2SO_2 + O_2 \rightarrow 2SO_3$ $SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow 2H^+ + SO_4^=$ $NH_3 + H_2O \rightarrow NH_4OH \rightleftarrows NH_4^+ + OH^-$	conversion rate $= 2.5$%/min	extrapolation to atmospheric conditions used to estimate conversion rate
Espenson and Taube 1965 (53)	SO_2 oxidation by Ozone	$SO_2 + O_3 + H_2O \rightarrow HSO_4^- + H^+ + O_2$ (in acid solution) $SO_3^= + O_3 \rightarrow SO_4^= + O_2$ (in basic solution)	not determined	
Scott and Hobbs 1967 (54)	SO_2 oxidation catalyzed by NH_3	SO_2, NH_3, CO_2 in equilibrium with ions and gas $SO_3^= + 1/2\ O_2 \rightarrow SO_4^=$	$\frac{d[SO_4^=]}{dt} = k[SO_3^=]$ $k = .0017\ sec^{-1}$	25°C only; k estimated from Van den Heuvel and Mason
Beilke and Georgii 1968 (55)	Washout and rainout of SO_2 and sulfate aerosols		assumed instantaneous oxidation of all SO_2 incorporated into droplet	calculated $SO_4^=$ concentrations from 0.3 to 36.5 mg/ℓ depending on rain rate and assumed SO_2 gas phase concentration
Foster 1969 (56)	SO_2 oxidation catalyzed by metal salts	$2SO_2 + 2H_2O + O_2 \xrightarrow{\text{catalyst}} 2H_2SO_4$	SO_2 conversion rate = .09%/min for Mn, .15 to 1.5%/min for Fe for typical input parameters	theoretical study; rates for Mn and Fe are functions of many factors; rate for Fe catalyzed oxidation is pH dependent
Matteson, Stober, and Luther 1969 (57)	SO_2 oxidation catalyzed by metal salts	$Mn^{2+} + SO_2 \rightleftarrows Mn \cdot SO_2^{2+}$ $2Mn \cdot SO_2^{2+} + O_2 \rightleftarrows [(Mn \cdot SO_2^{2+})_2 \cdot O_2]$ $\rightleftarrows 2Mn \cdot SO_3^{2+}$ $Mn \cdot SO_3^{2+} + H_2O \rightleftarrows Mn^{2+} + HSO_4^- + H^+$ $HSO_4^- + H^+ \rightleftarrows H_2SO_4$	$-\frac{d(SO_2)}{dt} = k_1[Mn^{2+}]_0^2$ $k_1 = 2.4 \times 10^5\ M^{-1}\ s^{-1}$	negligible $SO_4^=$ formation for RH <95%; similar mechanism may be responsible for catalysis by other metal salts
McKay 1971 (58)	SO_2 oxidation catalyzed by NH_3	same as Scott and Hobbs	$\frac{d[SO_4^=]}{dt} = k[SO_3^=]$; $k = (.013 + 59[H^+]^2)\ sec^{-1}$ $= .032\ sec^{-1}$ at neutrality (25°C)	considered variation with temperature; k estimated from Fuller and Crist; found large negative temperature rate correlation
Cheng, Corn, & Frohlinger 1971 (59)	SO_2 oxidation catalyzed by metal salts	$2SO_2 + 2H_2O + O_2 \xrightarrow{\text{catalyst}} 2H_2SO_4$	SO_2 conversion rate ∿.03%/min with Mn^{2+} levels typical of urban industrial atmosphere; ∿.33%/min with levels typical of plume from coal powered plant	oxidation rate estimated by extrapolation to atmospheric conditions
Miller and DePena 1972 (60)	SO_2 oxidation catalyzed by NH_3	similar to Scott and Hobbs	$\frac{d[SO_4^=]}{dt} = k[SO_3^=]$ $k \sim .003\ sec^{-1}$ (25°C)	k estimated by fit of experimental data to theoretical curves

TABLE 10. (CONTINUED)

AUTHOR	TYPE OF MECHANISM	ELEMENTS OF MECHANISM	RATE COEFFICIENTS AND/OR EXPRESSIONS	COMMENTS
Penkett 1972 (61)	SO_2 oxidation by ozone	$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$	$\frac{d(O_3)}{dt} = k_2(O_3)\ (HSO_3^-)$ $k_1 = 3.32 \pm .13 \times 10^5 M^{-1}s^{-1}$ SO_2 conversion rate $\sim .21\%$/min	9.6°C; SO_2 oxidation rate extrapolated from data; much faster than Scott and Hobbs
Chen & Barron 1972 (62)	Sulfite oxidation catalyzed by cobalt ions	free radical mechanism; Co(III) reduced	$-\frac{d(O_2)}{dt} = k\left[Co(H_2O)_6^{3+}\right]^{1/2}\left[SO^{3=}\right]^{3/2}$	could not determine specific value for k
Penkett and Garland 1974 (42)	SO_2 oxidation by ozone	$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$	$-\frac{d(SO_2)}{dt} = k\left[SO_3^{=}\right]$ $k = 4.18 \times 10^{-4} + 1.77\ [H^+]^{1/2}\ sec^{-1}$	pH range from 4 to 7 10°C; .1 ppm SO_2, .05 ppm O_3 in fog water
Brimblecombe & Spedding 1974 (63)	SO_2 oxidation by O_2 with trace Fe catalyst	complex	$-\frac{d[S(IV)]}{dt} = k[Fe(III)]\ [S(IV)]$ $k = 100\ M^{-1}\ s^{-1}$ SO_2 conversion rate $\sim 3.2\%$/day in fog assuming 28 $\mu g/m^3$ SO_2 and 10^{-7} M Fe(III)	Possibility of Fe(III) contamination discussed
Freiberg 1974 (64)	SO_2 oxidation catalyzed by Fe	complex	$\frac{d\left[SO_4^{=}\right]}{dt} = X_o K_s^2 [H_2SO_3]^2\ [Fe^{3+}]/[H^+]^3$ k_s = 1st dissociation constant of H_2SO_3	Rate increases rapidly with RH and decreases by about one order of magnitude with 5°C increase in temperature.

been either ammonia or a metal salt or oxide, most likely Fe(III) or Mn(II). (Some investigations have postulated reaction in the aqueous phase of a deliquescent aerosol particle; in mechanisms of this type, the classifications homogeneous and heterogeneous lose much of their meaning, and these reactions are rather arbitrarily included in this section of the report.) Aqueous phase oxidation of SO_2 by O_3 has recently been measured and reported. A very limited amount of work has been done on photochemically induced oxidation in the aqueous phase, but it is generally discussed as a side reaction in (and dependent upon) the photoxidation of olefins and reactive hydrocarbons. Because of the low output of these species from power plants, it is expected that photochemical oxidation of SO_2 in the aqueous phase is not a significant source of sulfates in power plant plumes.

The following discussion of the oxidation of SO_2 by O_2 in the aqueous phase will assume (unless otherwise stated) that the reaction is either

$$HSO_3^- + 1/2\ O_2 \rightarrow HSO_4^- \qquad \text{or}$$

$$SO_3^= + 1/2\ O_2 \rightarrow SO_4^= \quad .$$

It will be clear from the context which reaction is being discussed. This section of the report will consider first some general work on SO_2 oxidation in the aqueous phase, and then the specific effects of ammonia and metal salts. Finally, oxidation by ozone and photochemical processes will be discussed briefly.

In general, it should be reiterated that the aqueous phase oxidation of SO_2 is highly dependent on meteorological conditions, since even the fastest mechanism can produce no sulfate if there is no aqueous phase present. Furthermore, even when there is an aqueous phase present, scavenging efficiency, solubility, and diffusion must be considered. For these reasons, aqueous phase oxidation must be considered somewhat differently than gas phase oxidation when applied to power plant plumes.

Although oxidation of sulfite ions and "sulfurous acid" by oxygen was investigated as long ago as 1898 [65-74], much of this early work cannot be considered quantitatively since, among other things, there is often no record of purity precautions applied to regents. These works did show the oxidation to be a long chain reaction, and as such to be quite sensitive to both positive and negative catalysts (catalysis and inhibition), but the details of the mechanism are still uncertain. In his investigation of the effect of inhibitors on the reaction, Bäckström [70] found that his data fit the relation

$$v = A/(B+m)$$

(where v is the velocity of oxygen absorption, A and B are constants, and m is the inhibitor concentration) although deviations were noted for low values of m.

The earliest definitive work on the process was reported by Fuller and Crist[49] in 1941. In the absence of added catalyst, their data showed the reaction $SO_3^{=} + 1/2\ O_2 \rightarrow SO_4^{=}$ to be first order with rate constant $k_1 = 0.013 \pm 0.0015\ sec^{-1}$. The work was performed at 25°C with pure oxygen atmospheres. When the inhibitor mannitol was added, the data were found to fit an expression similar to Bäckström's, and over a wider range of inhibitor concentrations:

$$-\frac{d(SO_3^{=})}{dt} = \frac{A}{A + m} k_1 (SO_3^{=})$$

where A is about 10^{-5}. The catalytic effect of Cu^{++} was also investigated, and it was found that the data fit an expression of the form

$$-\frac{d(SO_3^{=})}{dt} = \left[k_1 + k_3 (Cu^{++})\right](SO_3^{=})$$

and k_3 was determined to be $2.5 \pm 0.33 \times 10^6\ \underline{M}^{-1}sec^{-1}$. The extreme sensitivity of the reaction to catalysis by Cu^{++} can be seen by noting that at concentrations greater $5 \times 10^{-9}\ \underline{M}$, $k_3(Cu^{++}) > k_1$. The effect on pH on the oxidation was also investigated, and as noted in previous (and subsequent) work, the oxidation rate increased with increasing pH (see Table 11 and Figure 5). This is consistent with the assumption that the sulfite rather than the bisulfite is the species being oxidized; the addition of H^+ shifts the equilibrium ($HSO_3^- \rightleftarrows H^+ + SO_3^{=}$) to

TABLE 11. EFFECT OF ACIDITY ON REACTION VELOCITY[49]

Hydrogen ion added, m/l	Time, sec.	Total Sulfite Concn., m/l	Sulfite ion Concn., m/l	pH	k_1
0.0032	0	0.0164	0.0132	5.92	1.9[a]
	20	.0129	.0097	5.77	5.4
	40	.0096	.0064	5.60	5.9
	60	.0072	.0040	5.40	6.3
	80	.0055	.0023	5.15	
.0065	0	.0160	.0095	5.47	6.3
	20	.0121	.0056	5.24	7.0
	40	.0094	.0029	4.96	6.6
	60	.0078	.0013	4.60	6.9
	80	.0069	.0004	4.09	
.0097	0	.0145	.0048	5.00	6.8
	20	.0119	.0022	4.66	7.2
	40	.0104	.0007	4.16	
.0130	0	.0160	.0030	4.66	7.6
	20	.0139	.0009	4.14	6.9
	40	.0131	.0001	3.19	
.0162	0	.0174	.0012	4.17	6.1
	20	.0164	.0002	3.40	
				Av = 6.6 = 0.47	

(a) This figure was not used in calculating k_1 (average).

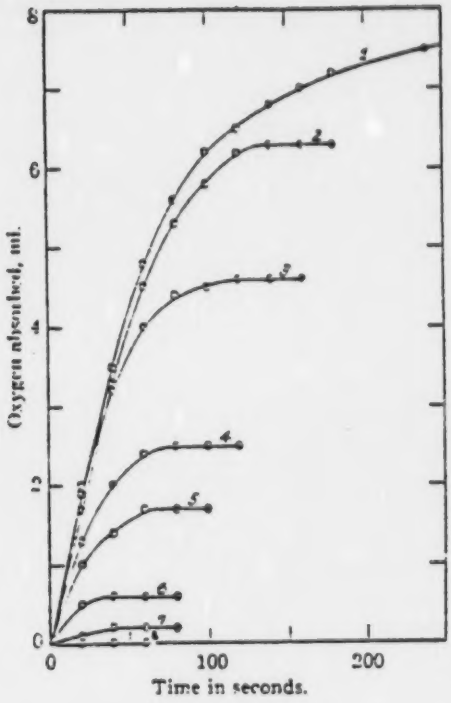


FIGURE 5. EFFECT OF ACIDITY (49)

Curves 1 to 8 refer respectively to 0.02 molar solutions of sodium sulfite to which 0, 0.0032, 0.0065, 0.0097, 0.0130, 0.0162, 0.0195, and 0.0325 mole per liter of hydrogen ion have been added as sulfuric acid.

the bisulfite side, decreasing the sulfite concentration. This effect leads to the expression

$$-\frac{d(SO_3^{=})}{dt} = \left[k_1 + k_4 \, (H^+)^{1/2} \right] (SO_3^{=})$$

where k_4 is found to be 6.6 ± 0.47 $\underline{M}^{-1/2}sec^{-1}$. This value is calculated assuming the second dissociation constant of sulfurous acid to be 5×10^{-6}; more recent research indicates this value is actually closer to 6.3×10^{-8}[75], leading to a better value of $k_4 = 59$ $\underline{M}^{-1/2}sec^{-1}$.

While the details of the chain mechanism responsible for the oxidation of SO_3 are not certain, work by Bassett and Henry[76] and Bassett and Parker[50] led to the conclusion that the uncatalyzed reaction proceeds *via* ionic complexes such as $(O_2 \cdot SO_3)^{2-}$ and $(O_2 \cdot S_2O_5)^{2-}$. The manganese ion-catalyzed reation was postulated to involve an intermediate such as $(O_2 \cdot Mn(SO_3)_2)^{2-}$ which could rapidly undergo self oxidation and reduction. The intermediates in the case of cobalt-, nickel-, and iron-catalyzed oxidation were assumed to be similar but less active complexes. Quantitative rate measurements were not performed in this study.

One of the first attempts to study the role of SO_2 oxidation in air chemistry was done by Junge and Ryan[51]. Their work showed

that the uncatalyzed reaction produced a negligible amount of sulfate, and that it was not photosensitive in normal sunlight. In the presence of a catalyst ($FeCl_2$) the sulfate formation was found to reach a limiting value after a period of time (typically one to three hours), and the final sulfate concentration depended linearly on the initial SO_2 concentration for a given catalyst concentration. Furthermore, it was found that the pH of the solution dropped during the course of the reaction, and that very little additional sulfate was formed once the pH reached 2.2.

Junge and Ryan also did a preliminary study to determine the effectiveness of various salts (at the same concentration by weight) as oxidation catalysts, and found manganese to be most efficient (see Table 12). This study was not meant to be exhaustive, however, and it should be kept in mind that in the atmosphere, the concentrations of various catalysts are not equal, and thus a less efficient (but more abundant) catalyst may actually be more important in sulfate production under true atmospheric conditions.

AMMONIA CATALYSIS*

Junge and Ryan investigated the enhanced effectiveness of metal catalysts in the presence of NH_3, and concluded that the NH_3

*It may be argued that promotion of the oxidation of SO_2 by ammonia is not catalysis in the true sense of the word; nevertheless, the term will be used for convenience in the following discussion with a less-than-formal definition.

TABLE 12. THE EFFECT OF VARIOUS SOLUTIONS ON SULFATE FORMATION[51]

Solution of 51 x 10^4 $\mu g/m^3$ SO_2 and		SO_4^{--} Concentration after 3 hr	
$MnCl_2$	(1 $\mu g/cm^3$)	329	$\mu g/cm^3$
$CuCl_2$	"	199	
$FeCl_2$	"	167	
$CoCl_2$	"	49	
NH_4OH	"	49	
NaCl	"	4	
dist. H_2O		3	

served to neutralize the sulfate formed in the reaction. Its role in maintaining a high pH and thus a high sulfite concentration is not mentioned, and this is probably a more important function. A theoretical investigation of the process in fog droplets estimated 2.9 $\mu g/m^3$ of sulfate would be formed in an atmosphere initially containing 20 $\mu g/m^3$ of SO_2 and 3 $\mu g/m^3$ of NH_3 ("clean country air") with a liquid water content of 0.1 g/m^3. The same fog in air polluted with 500 $\mu g/m^3$ of SO_2 and 10 $\mu g/m^3$ of NH_3 initially should form 26.2 $\mu g/m^3$ of $SO_4^=$, or nearly an order of magnitude more. No calculations were attempted for falling drops because of uncertainties regarding concentration behavior of the catalysts in such systems.

Experimental work on the formation of ammonium sulfate in water droplets was done by van den Heuvel and Mason[52]. Using water droplets suspended on a fiber grid and exposed to an airstream containing controlled amounts of SO_2 and NH_3, they found that the mass of salt (assumed to be ammonium sulfate) produced in the droplet is proportional to the surface area of the drop and to time. Because of certain problems with the technique, however, their results are only semi-quantitative. Furthermore, application of their results to the atmosphere requires extrapolation to much lower gas phase SO_2 and NH_3 concentrations than were used in the study. Allowing this extrapolation, their predicted rate dependence leads to a rather large conversion rate of about 2.5%/min in an atmosphere containing 100 $\mu g\ SO_2/m^3$ and

10 μg NH_3/m^3. Keeping in mind that the data are only semi-quantitative, it is still apparent that the process is of importance in the oxidation of SO_2 in droplets as well as in bulk solution.

A much-quoted theoretical investigation by Scott and Hobbs[54] assumes equilibrium is maintained between gaseous and dissolved SO_2, NH_3, and CO_2, and between the ions produced in the dissociation of the dissolved species:

$$SO_{2(g)} + H_2O \rightleftarrows SO_2 \cdot H_2O \qquad K_{hs} = [SO_2 \cdot H_2O]/P_{SO_2}$$

$$SO_2 \cdot H_2O \rightleftarrows HSO_3^- + H^+ \qquad K_{1s} = [HSO_3^-][H^+]/[SO_2 \cdot H_2O]$$

$$HSO_3^- \rightleftarrows SO_3^= + H^+ \qquad K_{2s} = [SO_3^=][H^+]/[HSO_3^-]$$

$$NH_{3(g)} + H_2O \rightleftarrows NH_3 \cdot H_2O \qquad K_{ha} = [NH_3 \cdot H_2O]/P_{NH_3}$$

$$NH_3 \cdot H_2O \rightleftarrows NH_4^+ + OH^- \qquad K_{1a} = [NH_4^+][OH^-]/[NH_3 \cdot H_2O]$$

$$CO_{2(g)} + H_2O \rightleftarrows CO_2 \cdot H_2O \qquad K_{hc} = [CO_2 \cdot H_2O]/P_{CO_2}$$

$$CO_2 \cdot H_2O \rightleftarrows HCO_3^- + H^+ \qquad K_{1c} = [HCO_3^-][H^+]/[CO_2 \cdot H_2O]$$

$$HCO_3^- \rightleftarrows CO_3^= + H^+ \qquad K_{2c} = [CO_3^=][H^+]/[HCO_3^-]$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = [H^+][OH^-]$$

Using the appropriate equilibrium expressions and constants, it is possible to derive an expression for the sulfite concentration as a function only of $[H^+]$, which can in turn be determined

by invoking a charge balance equation. The formation of sulfate can then be calculated by a simple integration of the assumed first-order oxidation rate equation

$$\frac{d[SO_4^{=}]}{dt} = k\,[SO_3^{=}] \ .$$

The rate constant k was taken to be 0.1 min^{-1} or 0.0017 sec^{-1} based on an analysis of van den Heuvel and Mason's data. The calculations made under these assumptions did not show the sulfate formation to reach an asymptotic limit in one to two hours as noted by Junge and Ryan, nor did it show the linear dependence on the initial partial pressure of SO_2. The work yields oxidation rates of the order of 2.5 percent per hour and does suggest sulfate levels of the same order of magnitude as some measurements[77], but the corresponding NH_4^+ concentrations and pH's are much higher than measured, and in general rather long times are required for large sulfate formation. Depletion of the gas phase concentrations of SO_2 and NH_3 was not considered.

Assuming the same set of reactions and equilibrium constants as Scott and Hobbs, McKay[58] was able to predict much faster formation of sulfate by calculating the first order rate constant from the expression given by Fuller and Crist:

$$k = 0.013 + 59[H^+]^{1/2} \ sec^{-1} \ .$$

At pH 7, this is 20 times as great as the value used by Scott and Hobbs, and at pH 5, it is 120 times as great. Furthermore,

the work indicated that the reaction should proceed faster as the temperature is lowered, a feature which had been noted by other investigators and may be attributed to increased gas solubility at lower temperatures. Some of McKay's data suggest rates of oxidation of about 13 percent per hour.

There is still no concensus about the "best" value for the oxidation rate for this system. Data taken by Miller and de Pena[60] fit a curve corresponding to $k \sim 0.003$ sec^{-1}, very close to the value used by Scott and Hobbs. Some of the Miller and de Pena curves, however, suggest oxidation of only 0.1 percent per hour.

The relevance of the entire SO_2-NH_3-water system to the case of power plant plumes is quite uncertain. Reported SO_2 oxidation rates attributable to ammonia catalysis vary widely, from 0.1 - 13 percent per hour. The NH_4^+ concentrations and pH calculated for the system, regardless of k, are much higher than measurements indicate. One possible explanation for this involves the solubility of NH_3 in water: if it is actually a good deal less than the models assume it is, both $[NH_4^+]$ and pH predictions could be lowered. This would mean lower $[SO_3^=]$ and thus, for the Scott and Hobbs-type analysis, the rate would be lower. For an analysis using McKay's formula for k, however, the lower pH also means a larger value for k, and for reasonable ambient levels of SO_2 and NH_3, the rate will actually increase.

The other point which must be kept in mind is the time required for appreciable oxidation. A fog or mist could be in the vicinity of a plume for times on the order of hours. Precipitation falling through a plume, however, does so in a matter of minutes or less. Thus, in order to contribute significantly to the sulfate formation in the aqueous phase, a mechanism must have a time constant* of the same order as the time that the phase is in contact with the plume.

METAL CATALYSIS

Concurrently with the above work on the SO_2-NH_3-water system, there have been several important studies on the effect of metal catalysts in the oxidation of SO_2. Work by Johnstone and Coughanowr[78] indicated that, for high catalyst concentrations, the oxidation could be assumed to occur within a spherical shell at the surface of the drop. This shell becomes thicker as the catalyst concentration decreases, or as the SO_2 concentration at the surface increases, and for some critical value of either parameter, of course, the entire drop is involved.

An excellent review and extension of the earlier theoretical work was given by Foster[56], whose interest was in the oxidation of SO_2 in power plant plumes. After a lengthy analysis of droplet (especially $MnSO_4$) growth, he considers the oxidation

*The time constant for a mechanism may be thought of as the half-life of the rate-limiting reaction.

rates by manganese and iron catalysts. In the case of iron catalysis, some of the assumptions made are based on the work of Nytzell-de Wilde and Taverner[79]. The derivation led to these rate expressions:

$$\text{Rate of } SO_2 \text{ oxidation by } Mn^{2} \text{ catalyst} = \frac{22.4\ K_i C_i^2 V}{10^{-6}\ GD} \times 10^2\% \text{ per min.}$$

$$\text{Rate of } SO_2 \text{ oxidation by } Fe^{2} \text{ catalyst} = 2.24 \times 10^3\ \frac{DWK_H(1 - f_o)K_i' n_i f_i}{[H^+]\qquad M_i}\% \text{ per min.}$$

where the symbols are defined in Table 13, as are typical values for each parameter. Using these values and assuming values for $[H^+]$, K_i and K_i', Foster estimates SO_2 rates of 0.09%/min for Mn and 0.15-1.5%/min for Fe, suggesting that iron oxides are the most important catalysts for aqueous phase SO_2 oxidation in plumes.

Matteson *et al.*[57] considered the kinetics of the oxidation mechanism using a manganese sulfate aerosol catalyst. A theoretical analysis of the mechanism (see Table 10) leads to the conclusion that the rate is proportional to the square of the initial aqueous Mn^{++} concentration (Foster had assumed a similar dependence in his calculation of the manganese-catalyzed rate). The rate constant was found experimentally to be $2.4 \times 10^5\ \underline{M}^{-1}s^{-1}$. It was also found that almost no sulfate is formed when the relative humidity is less than 95%, probably because the aerosol

TABLE 13. NOMENCLATURE AND VALUES USED FOR PLUME SO_2 OXIDATION CALCULATIONS[56]

	Nomenclature		Value
General	W	Effluent dust burden, g/l_{eff}	2×10^{-3}
	G	Effluent SO_2 content, ppm	$2{\cdot}5 \times 10^{3}$
	D	Effluent dilution factor	10^{-3}
	f_o	Fraction of total sulphur oxidized	10^{-1}
	S	Droplet suplhate concentrations, mol/l_{H_2O}	1
Manganese (Mn_3O_4)	M_i	Oxide molecular weight, g/mol	$2{\cdot}29 \times 10^{2}$
	n_i	Number of catalytic ions per molecule	3
	f_i	Fraction by weight of dust soluble	2×10^{-4}
Iron (Fe_2O_3)	M_i	as above	$1{\cdot}60 \times 10^{2}$
	n_i	as above	2
	f_i	as above	10^{-2}

is insufficiently hydrated. The authors feel that a similar mechanism may be involved where other catalysts are concerned, although no others were used in either the experimental work or theoretical development.

Further work on $MnSO_4$ and on $MnCl_2$, $CuSO_4$, and NaCl aerosols was reported by Cheng *et al.* [59]. In terms of catalytic efficiency, the following order was established: $MnSO_4$ > $MnCl_2$ > $CuSO_4$ > NaCl. In an attempt to extrapolate the experimental results to atmospheric conditions, they assumed a fog of 15 μm droplets containing 0.2 g H_2O/m^3 in which half of the droplets contain catalyst at concentrations capable of oxidizing SO_2 at the same rate as that found with 500 μg $MnSO_3/m^3$. Under these assumptions, the extrapolation of their experimental results indicated that SO_2 at the 0.1 ppm level should be oxidized at a rate of about 20%/hr. The level of catalyst here was taken to be typical of that in a power plant plume, and the resulting rate is about four times higher than the .09%/min determined theoretically by Foster.

A kinetic study of the homogeneous oxidation of SO_2 by cobalt ions was performed by Chen and Barron [62]. Although the value for the rate constant was not determined, the reaction was found to be zero order in oxygen, three halves order with respect to sulfite ion concentration, and one half order with respect to cobalt catalyst concentration. The mechanism proposed

to account for these features is a free radical chain adapted from "Backstrom"[70]:

$$SO_3^{=} + Co(H_2O)_6^{3+} \xrightarrow{k_1} Co(H_2O)_6^{2+} + \cdot SO_3^{-}$$

$$\cdot SO_3^{-} + O_2 \xrightarrow{k_2} \cdot SO_5^{-}$$

$$\cdot SO_5^{-} + SO_3^{=} \xrightarrow{k_3} SO_5^{=} + \cdot SO_3^{-}$$

$$SO_5^{=} + SO_3^{=} \xrightarrow{k_4} 2SO_4^{=}$$

$$\cdot SO_3^{-} + \cdot SO_3^{-} \rightarrow \text{inert products}$$

$$\cdot SO_3^{-} + \cdot SO_5^{-} \rightarrow \text{inert products}$$

$$\cdot SO_5^{-} + \cdot SO_5^{-} \xrightarrow{k_5} \text{inert products.}$$

It has been mentioned before that many of the studies on SO_2 oxidation have been done using rather high SO_2 concentrations, requiring a large extrapolation in order to apply the results to the atmosphere. Brimblecombe and Spedding[63] attempted to correct this situation by measuring the oxidation of SO_2 at concentrations of about 10^{-5} M in aqueous solutions with Fe(III) at abcut 10^{-6} M acting as the catalyst, using a radiochemical method of analysis. The sensitivity to the iron catalyst, even at these low SO_2 concentrations, is indicated by the fact that even in the purest water obtainable, the oxidation proceeded at a measureable rate, presumably due to trace iron at concentrations on the order of 10^{-8} M. They suggest that a free radical

mechanism similar to that above is responsible, with the initiator being FeOOH:

$$SO_3^{=} + FeOOH + 3H^+ \rightarrow Fe^{2+} + 2H_2O + \cdot SO_3^-$$

and the Fe(III) may be regenerated by oxidation of Fe^{2+},

$$\cdot SO_3^- + Fe^{2+} \rightarrow SO_3^{=} + Fe^{3+}$$

allowing oxidation of large amounts of SO_2 by very small amounts of Fe(III). (The hydrozylated Fe(III) species FeOOH has a higher oxidation-reduction potential than Fe^{3+} (0.908 V compared with 0.77 V)[75,80], and pH values in the range pH 4 to pH 5 tend to favor formation of the hydroxylated species. Thus, FeOOH appears to be a better oxidizing agent than Fe^{3+} for the production of $\cdot SO_3^-$ radicals).

In another study of the catalytic effect of iron, Freiberg[64,81] obtains a rate expression:

$$\frac{d[SO_4^{=}]}{dt} = \frac{K_T K_s^2 [Fe^{3+}] [H_2SO_3]^2}{[H^+]^3},$$

where K_s is the first dissociation constant for H_2SO_3 and K_T is a rather complicated function of $[O_2]$, $[Fe^{3+}]$, and several equilibrium constants; the expression fits the published data of

others[51,79]. The strong dependence of the rate in droplets on relative humidity is seen to be due to the increase in pH (by dilution) as the humidity increases.

Other Mechanisms

There have been few mechanisms proposed for the oxidation of SO_2 in aqueous systems other than the catalytic ones mentioned above. Work on a photochemical process in the aqueous phase was reported by Jones and Adelman[82], but as is typical of such mechanisms, the presence of reactive hydrocarbons is necessary. It is probably safe to say that photochemical processes are not important in the aqueous phase oxidation of SO_2 in plumes under ordinary circumstances due to the low concentrations of such hydrocarbons. The possibility of entrainment of such species must be considered, but kinetic studies of the aqueous phase photooxidation of SO_2 are virtually nonexistent. Of possibly greater importance are reactions with ozone ($HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$). Espenson and Taube[53] performed tracer experiments which, although they did not yield rate data, indicated that the reaction is not as simple as the stoichiometric relation above suggests, since oxygen atoms are exchanged with the solvent as well as being transferred between sulfite ions and ozone. Penkett[61], using ozone in the range of 3 to 5 x 10^{-6} M, found the oxidation of bisulfite to be first order with respect to ozone. The overall reaction was found to fit a rate expression of the type $-d(O_3)/dt = k_2(O_3)(HSO_3^-)$

and k_2 was found to be $3.32 \pm 0.11 \times 10^5$ $\underline{M}^{-1}s^{-1}$. This leads to an oxidation rate of about 0.21%/min in a cloud under typical conditions (10 °C, pH 5, about .1 to 1 g/m^3 liquid water content) assuming 7 ppb SO_2. The ozone level assumed, 50 ppb, represents yet another extrapolation of the laboratory data. This rate is some 70 times faster than that predicted by the analysis of Scott and Hobbs, although it is of roughly the same order as indicated by McKay's calculations, depending on the pH. Subsequent work by Penkett and Garland[42] measured the rate of oxidation of SO_2 by ozone in fogs formed in a chamber, and the measured rates agree with those calculated in the earlier work.

It may be noted that in the above review, little attempt has been made to reconcile the findings of various authors. This stems partially from a feeling of frustration because there is such a wide spectrum of results reported, and also because so little of the work which has been done so far has been directly concerned with the SO_2 in plumes. Even those studies which attempt to relate their findings to the case of polluted atmospheres are forced to make rather gross extrapolations from the data collected in the laboratory, and the diversity of the results is hardly surprising. On the other hand, if there is one fact which the literature does show well, it is that the oxidation of SO_2 in the aqueous phase is highly sensitive to several parameters, among which are pH, relative humidity, temperature,

and catalyst concentration, which leads to the expectation that the rate really is highly variable. Thus, the conclusions which do emerge from the works reported are mainly qualitative:

(1) Under favorable meteorological conditions, aqueous phase oxidation of SO_2 must be considered, and in some cases it may be the predominant mechanism.

(2) Power plant plumes are significant sources of the metals (especially manganese and iron) which are able to catalyze the oxidation.

(3) The influence of ammonia on the reaction is of particular importance, both in the formation of ammonium sulfate and in its ability to increase the reaction rate by maintaining a high pH.

(4) Ozone is a potentially important aqueous phase oxidizing agent for SO_2, although its importance in the early plume may be doubtful because of depletion by reaction with NO.

(5) Aerosols of $MnSO_4$ and other species may be important as sources of catalysts, as well as reaction sites when the aerosols are hydrated.

(6) Because of the highly sensitive nature of the reaction (or reactions) to existing ambient conditions, typical rates probably range from about 0.1 to 2.0%/min, although even higher rates may be possible.

SECTION VII

HETEROGENEOUS STUDIES

Considerable attention has been given to the use of catalysts, especially platinum catalysts, for converting SO_2 to SO_3 for sulfuric acid production. Most recently, platinum and some of the rare earth oxides have been considered further in their roles as automotive oxidative catalysts. In this instance, as in the oxidation that occurs in plumes, the motivation was not a search for improved catalyst efficiency, but rather to understand the role of the catalyst. A review of the extensive literature concerning the heterogeneous catalysis of SO_2 oxidation for sulfuric acid production[83] would not be generally relevent to the scope of this report since plume SO_2 concentrations are orders of magnitude below the levels used in acid processing; the kinetic concepts involved, however, should be comparable.

Figure 6 taken from Boreskov[84] presents a brief overview of the effectiveness of a number of catalysts for oxidizing SO_2 to SO_3 in sulfuric acid production. A most pertinent aspect of Boreskov's efficiency curves is the sharp drop in the conversion efficiency of the metal oxides at temperatures below 500°C. The catalysts most pertinent to plume oxidation shown here might be V_2O_5 and Fe_2O_3 (at much lower temperatures, of course) but as

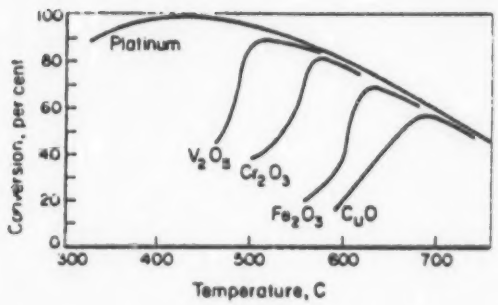


FIGURE 6. CONVERSION OF SO_2 TO SO_3 IN THE PRESENCE OF SEVERAL CATALYSTS (84)

will be brought out later, this drop-off in catalytic conversion efficiency may raise questions about the significance of heterogeneous gas-phase reactions in plumes.

It has generally been observed in fuel-burning processes that 1-2 percent of the sulfur in the fuel leaves the stacks as SO_3, and both heterogeneous and homogeneous reactions have been suggested to account for this result. Expressions developed by Calderbank[85] and by Kodles[86], respectively, indicate the rate of SO_2 oxidation to be negligible (< 3 ppm SO_3 per hour) at 300° K with 100 ppm SO_2:

$$r, \frac{\text{moles } SO_2 \text{ converted}}{\text{g catalyst-sec}} = \exp\left(\frac{31{,}000}{RT} + 12.07\right) \frac{P_{O_2} P_{SO_2}}{P_{SO_2}^{1/2}}$$

$$r = 1.76 \times 10^6 \exp\left(-\frac{32{,}414}{RT}\right)\left(N_{SO_2} \cdot N_{O_2}^{1/2} - N_{SO_3}\right)$$

Here the P's are in atmospheres, the N's are mole fractions, T is the absolute temperature (K) and R is the gas constant. This low rate tends to support earlier work[86] which shows that the conversion of SO_2 to SO_3 can occur homogeneously in the flame front (the reactive region of the flame) by stationary state processes:

$$SO_2 + O + M \rightleftarrows SO_3 + M$$

$$SO_3 + O \rightleftarrows SO_2 + O_2 \quad .$$

A recent study by Novakov, Chang, and Harker[87] presents evidence for the possible role of carbon (soot) particles as catalysts for the oxidation of SO_2 in the atmosphere. This evidence is

derived from electron spectroscopy for chemical analysis (ESCA) studies of particulate matter from a premixed hydrocarbon flame with different SO_2 levels. The ESCA spectrum of graphite particles exposed to SO_2 revealed peaks corresponding to sulfate and sulfide. Experiments varying the level of SO_2 added to the flame as well as the humidity of the air used also showed an increase in sulfate with increases in each of these parameters. Although the results of this study show a consistency for carbon acting as a catalyst, the evidence presented is somewhat limited. Also, there are no rate data presented in this study from which one might evaluate the significance of soot in plumes as a sulfate catalyst.

Corn and Cheng[88] have also carried out studies on the adsorption of SO_2 by activated charcoal, as well as by Fe_2O_3, MnO_2 and suspended particulate matter. In these experiments, packed beds of Teflon beads were coated with micron and submicron size aerosol particles, the beads were packed in a reactor, and progress of the reaction was followed by continuously monitoring the effluent SO_2. Activated charcoal yielded steady-state rates of conversion, or adsorption, of 0.013 and 0.021 μg SO_2/min/mg charcoal at SO_2 concentrations of 8.0 and 14.4 ppm, respectively. The experiments do not distinguish, however, whether the SO_2 underwent steady-state conversion in the reactor or whether there was catalyzed oxidation on the surface.

In the Fe_2O_3 experiments there was rapid interaction with SO_2, even at zero relative humidity. In the cases of Fe_2O_3, MnO_2 and suspended particulate matter there was evidence for significant physical adsorption of SO_2. In all cases, humidity increased the adsorptivity of SO_2.

Several species were inert to SO_2, i.e., did not adsorb SO_2; these were $CaCO_3$, V_2O_5 and flyash. The V_2O_5 results appear unusual since V_2O_5 is a recognized oxidation catalyst for SO_2. At 500° C and above, it is presumed to oxidize *via* the reaction:

$$SO_2 + V_2O_5 \rightleftarrows SO_3 + V_2O_4.$$

At room temperature, however, the sorption of SO_2 was only 1.2% at 95 percent relative humidity.

A number of other studies have also been conducted on the interaction of SO_2 with the iron oxides Fe_2O_3 and Fe_3O_4. In general, these studies have limited applicability to resolving the problem of reactions in plumes in that rate information is limited. Chun and Quon[89] carried out a study designed to measure the capacity of ferric oxide particles to oxidize SO_2 in air. The procedure used involved laying down a film of Fe_2O_3 on a filter (by combustion of iron carbonyl vapor) and passing a stream of SO_2 in air through the filter-reactor. The authors describe the reaction as a "capacity-limited heterogeneous reaction", because the reaction is not catalytic in the true sense of the term.

Active sites on the surface of the particles become occupied by the products of the reaction, and thus are not available for further reaction. The capacity of the Fe_2O_3 particles to oxidize SO_2 in air was found to be 62.6 µg/mg Fe_2O_3. The rate constant for the heterogeneous reaction was 9.4×10^{-3} ppm^{-1} min^{-1} (6.3×10^{-18} cm^3 $mole^{-1}$ sec^{-1}). SO_2 concentrations in this study were varied from 4.7-18.8 ppm and relative humidity was varied from 50-94 percent. The rate constant did not appear to be correlated with SO_2 or relative humidity.

Urone *et al.*[90] examined the reactions of SO_2 in the presence of hydrocarbons, nitrogen dioxide, moisture, particulate matter and ultraviolet radiation. Gaseous mixtures did not react in the dark and SO_2 oxidation was of the order of 0.1%/hr under ultraviolet irradiation. In the presence of particulate matter, the reaction was significant in some instances.

Table 14 presents a summary compilation of SO_2 conversion rates drawn from the Urone study. SO_2 concentrations in this study were varied from 8 - 14 ppm; particulate loadings were 16 - 30 mg. The results show high reactivity with the iron, lead and calcium oxides and low reactivity with NaCl, $CaCO_3$, Al_2O_3 and V_2O_5. The results compare well qualitatively with those of Corn and Cheng[88], who reported high reactivity for Fe_2O_3 and low reactivity for $CaCO_3$ and V_2O_5.

TABLE 14. SUMMARY OF SO_2 REACTIONS ON VARIOUS PARTICULATE SPECIES[90]

Particulate Species	% SO_2 Reacted/min
$CaCO_3$	.004-.07
Cr_2O_3	.009
V_2O_5	0-.015
NaCl	0-.02
Al_2O_3	.04
CaO	1.8-3.0
Al_2O_3/CaO	2.4-2.6
PbO	1.9
PbO_2	5.9
Fe_3O_4	4.2
Fe_2O_3	4.5

Smith, Wagman and Fish[91] report sorption studies of SO_2 on Fe_3O_4, Al_2O_3 and platinum, using particles ranging in size from about 0.01 to 0.1 micron diameter. Using a $^{35}SO_2$ technique, they developed sorption isotherms. Their technique may prove useful in distinguishing layers of preferential chemical adsorption from multilayers of physical adsorption. They observe significant adsorption on all three surfaces, but do not measure oxidation rates in these studies.

Some basic studies on the adsorption and conversion of SO_2 on CaO and MgO have been carried out as part of efforts to remove SO_2 from power plant stack gases by adding limestone or dolomite. Two studies from investigators at New York University[92,93] have been concerned with infrared examination of SO_2 adsorbed on CaO and on MgO. Sulfites are produced on the surface and subsequently oxidize to sulfates on heating in air.

Lunsford has also studied the SO_2-MgO system, both at high temperatures and at ambient temperatures[94]. The low temperature study, although it provides no rate data, has more potential relevance to plume chemistry. Samples of MgO and $Mg(OH)_2$ were exposed to SO_2 at 25 torr, and electron paramagnetic resonance (EPR) and infrared (IR) spectra were obtained. The results showed that heterogeneous oxidation occurred on the MgO particles. Sulfite ions and monodentate sulfite complexes were identified. The investigators suggest that water adsorbed with the SO_2 increases

the concentration of these ions on the surface, thus promoting the conversion rate.

A study of the macroscopic properties of SO_2 adsorbed on manganese oxides[95] is presented here mainly because of its relevance to the catalytic role of Mn in aqueous systems discussed in a previous section. This study looked at the adsorptive capacity of wet and dry MnO_2 and Mn_2O_3. Essentially, the study shows the increased capacity for adsorption with increasing surface area and decreasing specific gravity, both of which result from the absorption of water.

A study by Happel and Hnatow[96] is of interest here in relation to some of the preceding studies. A theoretical analysis of the use of the isotopic tracers $^{18}O_2$ and $^{35}SO_2$ in the catalytic oxidation of SO_2 over V_2O_5 catalyst suggests that in conversion reactions in commercial acid plants and stack gas converters, V_2O_5 is considerably more effective than in plumes. The study concluded that oxygen chemisorption is the limiting mechanistic step, with SO_3 desorption being of next importance in the rate control. A rate equation is derived for conditions near equilibrium. It appears, however, that the rate equation is not applicable to ambient, possibly non-equilibrium conditions in a plume. The analysis is useful, however, as a guide to investigators applying isotopic tracers (e.g., Urone[90] and Smith[91]).

In summary, the heterogeneous solid catalyzed gas phase oxidation studies carried out to date are of very limited usefulness to plume chemistry calculations. First, the literature is essentially void of reaction rate and/or mechanism studies relating (dry) heterogeneously catalyzed SO_2 oxidation systems to atmospheric processes. As pointed out in the previous section on aqueous phase oxidation systems, the most effective catalysis occurs in solution. The studies of Corn and Cheng[88] and Urone[90] raise an interesting point on the lack of reactivity of dry particulate vanadium. Because of the recognized activity of V_2O_5 as an acid catalyst,[97,98] it is often stated that high sulfate levels in some areas may be attributable to the use of vanadium-containing fuels. It would appear from these ambient temperature investigations, however, that if SO_3 is produced in the combustion process, or at least near the stack outlet, the vanadium-containing particulate matter is not responsible for excessive sulfate formation in plumes or in the atmosphere in general.

SECTION VIII

MODELLING APPLICATIONS

As suggested in the previous sections of this report, the measurement of SO_2 removal and/or sulfate formation rates, whether in the field or in the laboratory, presents a variety of problems. While the details of using these data in a model to predict sulfate formation are likewise formidable, the technique itself is at least conceptually uncomplicated. The third report to be prepared for this project will be the more detailed documentation of an actual model, STRAC (Source-Transport-Receptor Analysis Code), developed for this purpose.

The technique, in general, must create the model-world analog of a real-world situation through a suitable mathematical formalism. The practical limitations dictated by computer capacity and cost, as well as the more philosophical ones imposed by an imperfect knowledge of nature, of course, determine how good the analogy is. A model of a reactive power plant plume must include a means for calculating the spatial distributions of pollutants, and it is this portion of the modelling which involves chemical reaction data. Specifically, the model is defined by the general continuity equation for each of n chemical species (SO_2, SO_3, NO, O_3...):

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot(\vec{v}_i c_i) + r_i \qquad (i=1,2,\ldots n) \quad ,$$

where c_i is the concentration and r_i the rate of production of species i in a differential volume element of atmosphere. The rates r_i, of course, will in general be functions of temperature, relative humidity, insolation, and concentrations of all species. The solutions which yield values for the c_i's are generally found by finite difference methods, necessitating rather careful consideration of the technique to be applied, a subject beyond the scope of this report. The inclusion of chemical reaction mechanisms, however, is rather simple since chemical rate equations are naturally expressed as differential equations, the form required by the continuity equation.

The program which performs such model calculations can be made extremely versitile by separating the various functions into different subprograms. For example, in a simple case, the main program may handle the input/output functions and define such parameters as the initial calculation point and concentrations, and step size. A replacable segment may then be called to perform the finite difference integration, where the necessary derivatives are calculated in yet another subprogram. This allows the examination of different models by the simple replacement of one subprogram, rather than rewriting the entire code. In such a configuration, of course, one could also replace the finite difference method without disturbing the rest of the program, if such a replacement were desirable.

The actual inclusion of chemical rate data into a plume model, then, is not a great problem. The major obstacle to the use of such models is the difficulty of finding reliable data to use for input, since the result of any calculation can be no better than the assumptions and data upon which it was based. As the preceding sections point out, data available concerning SO_2 oxidation rates are not extensive, especially for heterogeneous gas phase processes, a fact which severly limits the immediate use of models as predictive tools. There are perhaps more important uses for them as diagnostic tools in the intercomparison of various mechanisms. It can be hoped that future studies will improve our understanding of the important SO_2 oxidation process and allow more informative diagnostic plume modelling than presently possible.

SECTION IX

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SECTION X

APPENDIX

THERMODYNAMICS AND KINETICS: A REVIEW

Because of the volume of material covered by this report, little attempt has been made to rigorously define the more common chemical terms or to discuss kinetic and thermodynamic concepts. It is hoped, however, that this material will be useful to the non-chemist. This section is intended to review basic kinetics and thermodynamics for these readers, and to simultaneously define some of the more general terms and concepts used throughout the report, for the sake of completeness. A more detailed discussion of thermochemical kinetics than the necessarily brief overview presented here may be found in any textbook on physical chemistry. It is essential to remember that the primary factor determining whether molecular or atomic species will react is their energy; species having lower energy are favored, and all reacting systems will tend toward configurations having the lowest possible potential energy. This behavior can be illustrated in terms of the bimolecular reaction,

$$A + B \rightarrow C + D$$

whereby reactants A and B are converted to products C and D. Figure 7 shows how the potential energy of the system varies with a parameter called the reaction coordinate, which indicates the

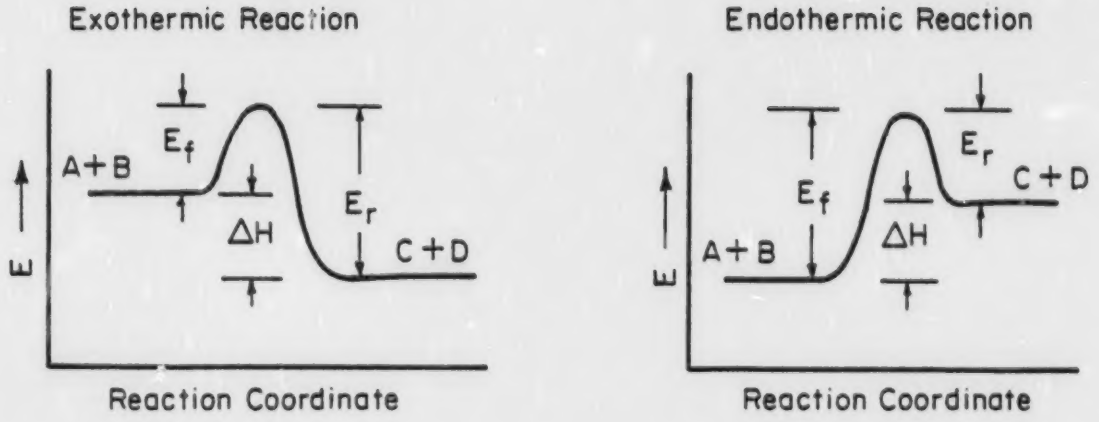

FIGURE 7. HYPOTHETICAL POTENTIAL ENERGY--
REACTION COORDINATE DIAGRAMS

degree of completion of the reaction. Moving from left to right, the initially separated molecules A and B approach and collide, increasing the potential energy of the system until a maximum is reached, and then separate forming products C and D. If the energy of the products is lower than the energy of the reactants, the first figure is appropriate and the reaction is termed <u>exothermic</u>; otherwise it is <u>endothermic</u> as shown in the second figure. The amount of energy gained (or lost) by the system during the course of the reaction is called the <u>enthalpy</u>, denoted ΔH is negative for exothermic reactions; reactions of this type correspond to lower energy of reaction products and thus, are said to be "favored" energetically.

Because of the presence of the maxima, or "energy barriers" in the figures, all collisions between A and B do not result in reactions. If a collision is not sufficiently energetic to reach the top of the energy barrier, the molecules must separate and remain as A and B; in fact, even with enough energy input, there is still a chance that the necessary rearrangements will not take place to allow the formation of products. The height of the energy barrier is called the <u>activation energy</u> of the reaction, labled E_f. The action of chemical species called <u>catalysts</u> can thus be understood: without reacting themselves, they provide a means whereby E_f can be lowered, allowing less energetic collisions to pass over the energy barrier. Figure 7 also reveals that with sufficient energy, C and D should be able to react to

form A and B; that is, the reverse reaction:

$$C + D \rightarrow A + B$$

is possible. Furthermore, the enthalpy of this reaction is simply $- \Delta H$, and the activation energy $E_r = E_f - \Delta H$. (Here the subscripts f and r denote reference to the forward and reverse reactions, respectively.)

It should be noted that the discussion above is not limited to bimolecular reactions. The concepts involved are rather easily generalized to more complicated systems, and also apply to the simpler unimolecular reactions. The latter class includes the extremely important photochemical reactions, which are initiated by electromagnetic radiation and are involved in many atmospheric processes.

It must be remembered that the above discussion was a gross simplification of the systems in which we are usually interested, systems which actually contain large numbers of atoms and molecules. In particular, atmospheric proceses generally involve reactions of pollutants at concentrations on the order of parts-per-billion or more, meaning some 10^{10} or more molecules/cm^3 of reactive species and more than 10^{19} molecules/cm^3 of inert species. Thus, the reactant molecules have a distribution of kinetic energies which are dependent on the temperature, and in such systems, it is possible to determine a rate at which each species is converted; the rate is

dependent on the amount of material present. For example, in the reaction A + B → C + D, A and B are converted, and

$$(d[A]/dt)_f = (d[B]/dt)_f = -k_f[A][B]$$

where the brackets denote concentrations. Similarly, A and B are both produced by the reverse reaction, (C + D → A + B), so

$$(d[A]/dt)_r = (d[B]/dt)_r = +k[C][D]$$

and the overall rate of change of A and B is

$$d[A]/dt = d[B]/dt = k_r[C][D] - k_f[A][B] \quad .$$

In the same way,

$$d[C]/dt = d[D]/dt = k_f[A][B] - k_r[C][D] = -d[A]/dt \quad .$$

The rate constants k_f and k_r can generally be expressed in the Arrhenius form:

$$k_f = M \exp(- E_f/RT)$$
$$k_r = N \exp(- E_r/RT)$$

where M and N are constants with only small temperature dependences, E_f and E_r are the molar activation energies for the forward and reverse reactions, respectively, and R and T are the gas constant (1.98 cal/mole-°K) and the absolute temperature. The exponential term reflects the kinetic energy distribution of the reacting molecules, that is, the probability that collisions will be sufficiently energetic to overcome the activation energy

requirements. The units of k_f and k_r, and thus M and N, are (concentration)$^{1-r}$ t^{-1}. The reaction order r is the total number (possibly fractional) of atoms or molecules; in the general case described here, r=2 for both the forward and reverse reactions. If, however, reactant A is present in such great quantities compared to B that its concentration remains virtually constant, A may be combined with k_f so that

$$(d[B]/dt)_f = -k_f[A][B] \approx -k_f'[B] \quad .$$

Here, although the reaction is actually second order, a pseudo-first order rate expression with constant k_f' can be applied. Such approximations are often valid in the atmosphere, especially when a trace substance is oxidized by oxygen, a major constituent.

The half-life of a species is the time required for half of it to react. In the special case of a first order (or pseudo-first order) reaction, this time is simply (ln 2)/k, where k is the rate constant. This quantity is often used to compare speeds of competing reactions.

If the reaction is allowed to proceed undisturbed for a long enough time, a state of dynamic equilibrium will be established when the rate of the forward reaction is exactly equal to the rate of the reverse reaction. That is, although both reactions are still proceeding, there are exactly as many molecules of each species formed by one reaction as are destroyed by the other. Thus,

$$k_f[A][B] - k_r[C][D] = 0 \quad .$$

In this case we can write an equilibrium expression for the reaction,

$$A + B \rightleftarrows C + D$$

and define an equilibrium constant:

$$K = \frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} \quad .$$

From the preceeding discussion, it is essential to realize that chemical conversion in macroscopic systems can be limited by either or both kinetic and thermodynamic factors. The kinetic factors are essentially determined by the energy available to the system: if only the most energetic collisions are able to culminate in reaction because of a high activation energy, the rate will be slow. Kinetic barriers can be overcome either by providing more energy to the system (usually as heat) or by applying an appropriate catalyst to lower the activation energy of the system. The thermodynamic factors are related to the equilibrium state of the system, and are somewhat more difficult to manipulate in situations where they are rate limiting. Because they only influence the activation energy, and not the equilibrium composition, catalysts are unable to affect the thermodynamic factors. The equilibrium constant is a function of temperature and can be determined from the definitions given previously:

$$K = \frac{k_f}{k_r} = \frac{M}{N} \exp\left(\frac{E_r - E_f}{RT}\right) = \frac{M}{N} \exp\left(\frac{-\Delta H}{RT}\right) \quad .$$

This indicates that K decreases with increasing temperature for an exothermic reaction.